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Field investigation of the impact of ventilation and temperature and development of an emission test cell for in situ measurements

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BY
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DISSERTATION SUBMITTED 2016

AALBORG UNIVERSITY
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Dissertation submitted

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Preface

This PhD-thesis is the result of approx. 4 years part time, corresponding to 3 years full time, research. The research was carried out in the period from January 2 2012 to February 12, 2016 at Department of Construction and Health, Danish Building Research Institute, Aalborg University Copenhagen (AAU CPH), with Professor Lars Gunnarsen and Senior Researcher Helle Vibeke Andersen as supervisors. During the external stay at the National Research Centre for the Working Environment and until completion of the thesis Per Axel Clausen supervised as well. Real Dania (2/3) and AAU (1/3) provided the funding for this study.

I am very grateful for the support of my supervisors; Professor Lars Gunnarsen for providing me this opportunity and for believing in me, Senior Researcher Helle V. Andersen for her tremendous work on improving my manuscripts and countless helpful and knowledge broadening theoretical discussions and Senior Researcher Per Axel Clausen for his great enthusiasm, tremendous support and for bringing me much motivation and knowledge.

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Copenhagen, 2016

Nadja Lynge Lyng

Abstract

Polychlorinated biphenyls (PCBs) are a group of chemicals that were commercially produced from 1929 and used among others as plasticisers. PCBs were added to building materials such as caulks and paints until they were banned in such uses in the late 1970s due to their environmental toxicity. In recent years, the concern about the presence of PCBs in buildings has risen. Measurements performed in several countries have shown that in some cases PCBs in the indoor air are at levels believed to be harmful to occupant's health. In 2009, Danish Health Authority issued guideline action values for PCB concentrations in indoor air.

The objective of this thesis was to investigate the effect of ventilation and temperature on the level of indoor PCB concentrations and to develop a low-cost method to measure PCB-emission rates from indoor building surfaces in situ.

The effect of ventilation and temperature was investigated by analysis of existing field data and by performing intervention studies in contaminated buildings. In 26 different rooms, where the PCB concentration had been measured prior to and after a change in air exchange rate, concentrations was in average reduced by 51% after the ventilation rate was increased. In the ventilation intervention studies concentrations decreased 30-46% when air exchange rates were changed from 0.2 to 5.5 h^{-1} in one classroom and from 0.5 to 6.6 h^{-1} in two bedrooms. Emission rates were found to increase linearly with increasing air exchange rate in the two bedrooms where the air exchange was increased incrementally. Thereby the increased emission rates reduce the effect of the ventilation.

Increased temperature was found to increase concentration exponentially in field data from one year of measurements in a contaminated apartment. Concentrations also increased exponentially during an intervention study in a contaminated bedroom where temperature was changed incrementally to six different levels between 20 and 30 °C. With a certain set of assumptions the variation in concentrations due to indoor air temperatures could be predicted by Clausius-Clapeyron Equation together with at least one measurement of concentration and temperature measured simultaneous.

A low-cost emission test cell was developed and proved capable of providing a micro environment where source potentials of individual surface areas (of up to 0.15 m^2) could be characterized. Sorption on cell surfaces did not affect measurements after 2-4 days; hence emission rates could be determined within a few days. PCB-emission rates were different depending on the surface type, even for different surfaces within the same room. The emission test cell can be used to prioritise future or evaluate completed remediation measures of contaminated surfaces.

Resumé

Polyklorerede bifenyler (PCB) er en kemikaliegruppe, som blev produceret kommercielt fra 1929 og er blandt andet anvendt som blødgørere. PCB blev tilsat byggematerialer såsom fugematerialer og malinger frem til, at de blev forbudt i åbne anvendelser i slutningen af 1970'erne på grund af deres skadelige effekter på miljøet. I løbet af de seneste årtier er der fundet PCB i bygninger, hvilket i nogle tilfælde har givet anledning til forhøjede PCB-koncentrationer i indeluften på niveauer, som menes på sigt at udgøre en sundhedsfare for mennesker. I 2009 fastsatte Sundhedsstyrelsen vejledende aktionsgrænser for PCB-koncentrationen i indeluften.

Formålet med dette studie var at undersøge betydningen af ventilation og temperatur for PCB-koncentrationen i indeluften og at udvikle en prisbillig metode til at måle emissioner fra indendørs overflader i bygninger.

Betydningen af ventilation og temperatur blev undersøgt ved at analysere eksisterende data fra felten og ved at udføre interventionsstudier i forurenede bygninger. PCB-koncentrationen var blevet målt før og efter en stigning i luftskiftet i 26 rum. Den gennemsnitlige reduktion af koncentrationen som følge af øget ventilation var på 51 %. I ventilationsinterventionsstudiet faldt koncentrationerne 30-46 %, når luftskiftet blev øget fra 0,2 til 5,5 h^{-1} i et klasseværelse og fra 0,5 til 6,6 h^{-1} i to soveværelser. Emissionen steg lineært med stigende luftskifte i de to soveværelser, hvor ventilationen blev øget trinvist. Stigningen i emissionen modvirkede dermed den reducerende effekt af øget ventilation.

PCB-koncentrationen, som blev målt over et år steg eksponentielt med øget temperatur i en forurenet lejlighed. Ligeledes steg koncentrationen eksponentielt under et interventionsstudie i et forurenet soveværelse hvor temperaturen gradvist blev ændret i seks niveauer mellem 20 og 30 °C. Under visse forudsætninger kunne variationen i luftkoncentrationen på grund af ændret indelufttemperatur forudsiges ved hjælp af Clausius-Clapeyron-ligningen og mindst en samtidig måling af koncentration og temperatur.

En prisbillig emissiontestcelle blev udviklet, og cellen var i stand til at skabe et lille afskærmet miljø, hvori de enkelte overfladers emissionspotentiale kunne karakteriseres (arealer op til 0,15m^2). Adsorption på overfladerne i cellen påvirkede ikke målingerne efter 2-4 dage og PCB-emissionerne kunne derfor bestemmes inden for få dage. PCB-emissionsniveauet var forskelligt afhængigt af overfladetypen, selv for forskellige overfaldetyper i det samme rum. Emissionstestcellen kan bruges til at prioritere fremtidige afhjælpningstiltag og vurdere afsluttede afhjælpningsmetoder af forurenede overflader.

List of original papers

The present thesis is based on the papers listed below. The papers will be referred to in the flowing text by the Roman numerals, Paper I – IV.

I. Nadja Lynge Lyng, Niels Trap, Helle Vibeke Andersen and Lars Gunnarsen. Ventilation as mitigation of PCB contaminated air in buildings: Review of nine cases in Denmark. Proceedings of the 13th Indoor Air conference in Hong Kong 2014

II. Nadja Lynge Lyng, Lars Gunnarsen and Helle Vibeke Andersen. The effect of ventilation on the indoor air concentration of PCB: An intervention study. Building and Environment 95: 305-312, 2015

III. Nadja Lynge Lyng, Per Axel Clausen, Claus Lundsgaard and Helle Vibeke Andersen. Modelling the impact of room temperature on concentrations of polychlorinated biphenyls (PCBs) in indoor air. Chemosphere 144:2127-133, 2016

IV. Nadja Lynge Lyng, Lars Gunnarsen, Helle Vibeke Andersen, Vivi Koefoed-Sørensen and Per Axel Clausen. Measurement of PCB emissions from building surfaces using a novel portable emission test cell. Building and environment 2015, *Resubmitted*

Indhold

1 Introduction

In Denmark, buildings contaminated with polychlorinated biphenyls (PCBs) became recognized as a possible health risk for the building occupants in 2009 (Gunnarsen et al., 2009). In 2009, Danish National Board of Health issued guideline action levels of PCB concentrations in indoor air, above which remediating measures are advised in order to protect human occupants against the health risk associated with prolonged exposure to PCBs (DK NBH, 2011; DK MEB, 2011). Elevated concentrations of PCBs in indoor air originate from emission of PCBs from certain building materials such as caulks, ceiling tiles, floor materials and paints which were manufactured between 1930s until the prohibition of such usage in late 1970s in most countries (Namieśnik et al. 1992; Fromme et al. 1996; Bergsdal et al. 2014; Scott and Snyder 2015).

With the recognition of the problem with PCBs in buildings arise needs for determination of the extent of the problem and knowledge on how to remediate efficiently. In contrast to many other contaminants in buildings, PCBs have the ability to spread from the original source over time due to the characteristics as semivolatile organic compounds (SVOC). This result in a contamination of not only the air but also other indoor materials (Weschler and Nazaroff, 2008); thereby creating further challenges to ensure the health of building occupants. Simple removal or encapsulation of the original materials containing PCBs has proven insufficient in several published and unpublished cases (Benthe et al., 1992). Interim remediation as well as characterisation of sources and their individual contribution to the indoor air concentration of PCB are therefore of great importance in decision making concerning effective remediation and in protection of occupants in contaminated buildings.

1.1 Objectives

The major aim of this thesis was to expand knowledge on remediation of PCB contaminated buildings with regard to elevated PCB concentration in indoor air. This comprehensive aim was focused in the following three objectives:

- *Investigate whether increased ventilation could reduce concentrations of PCBs in indoor air of contaminated buildings*
- *Investigate the effect of temperature on PCB concentration in indoor air*
- *Develop a method to characterise emission rates from different sources of PCBs in contaminated buildings in order to prioritise remediation measures*

The impact of ventilation and temperature was determined by field intervention studies and furthermore by reviewing and analysing available data from

contaminated buildings. The method to characterise emission rates was based on development of an emission test cell.

The hypotheses were:

- Increased ventilation can reduce indoor air concentrations and work as a mitigating measure
- Increased ventilation increase emission rate of PCBs to indoor air
- Increased source and air temperatures indoors increase the PCB concentration in indoor air
- A major part of the impact of indoor air temperature on air concentration can be estimated by Clausius-Clapeyron equation
- PCB-emission rates from building materials can be measured in an in situ emission test cell developed at low-cost
- Emission rate measurements can determine source strength of PCB containing building materials and help prioritise and control remediation measures

2 Background

Polychlorinated Biphenyls (PCBs) are a non-naturally occurring and man-made group of chemicals. PCBs was synthesized as early as 1864 (Griess, 1864) and industrially produced from 1929 (Bergsdal et al., 2014), where the cost of biphenyl decreased due to development of a commercial process (Jenkins et al., 1930). The group of chemicals has the structure of biphenyl with one to ten chlorine atoms replacing the hydrogen atoms positioned at 2 to 6 and 2´ to 6´ in Figure 2.1.

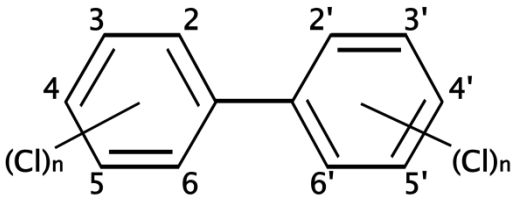


Figure 2.1 General chemical structures of polychlorinated biphenyls.

The structure of the biphenyl molecule allows 209 possible combinations of attached chlorine, congeners, with different physical-chemical properties and toxicity, depending on the number of chlorine atoms and their location.

2.1 Commercial PCB products

Commercial PCB-mixtures consist of different mixtures of the various congeners. The PCB mixtures were sold under different trade names in different countries followed by different numbering. Technical PCB mixtures with a chlorine content of 50-54% were sold by trade names such as Aroclor 1254 (U.S.), Clophen A50 (Germany), Phenclor dp5 (France) and Kaneclor-500 Japan) (de Voogt and Brinkman, 1989; Breivik et al., 2002). Around 150-180 different congeners are believed to have been produced commercially by a catalytic process of chlorination of biphenyl (de Voogt and Brinkman, 1989; Frame et al., 1996).

The PCB mixtures are viscous oily liquids, odour- and tasteless, with a clear to pale-yellow colour (Figure 2.2). The chemicals are insoluble in water and lipophilic. Among the desired properties and reasons for adding PCBs in various products are: high thermal conductivity, low electrical conductivity, resistance to oxidation, durability, elasticity and fire resistance (Mullin et al., 1984, de Voogt and Brinkman, 1989).

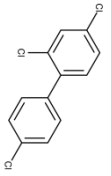
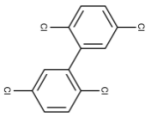
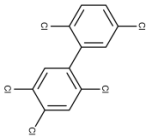
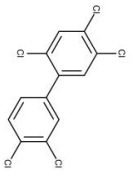
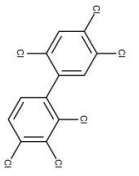
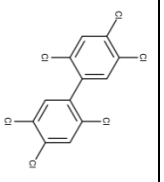
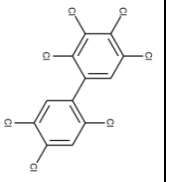
Figure 2.2 Technical PCB mixture with a congener composition similar to Aroclor 1248.

2.2 Indicator PCBs and their physical-chemical properties

For chemical analysis six indicator or marker PCB congeners have been selected; PCB-28, PCB-52, PCB-101, PCB-138, PCB-153, and PCB-180. These six congeners span a range of three to seven chlorines per molecule and are among the most abundant in commercial PCB mixtures (VDI, 2009). PCB-118 was added as an indicator PCB later than the rest, and was added in order to represent the dioxin-like PCBs as recommended in Heinzow et al. (2007). As a measure of the total amount of PCBs (PCB_{total}) in a sample, the sum of the seven indicator PCBs is multiplied by a factor specific for the PCB congener composition in the material sample. For air samples and material samples with congener composition different from known commercial mixtures the factor is set to 5 (de Boer and Dao 1991; VDI 2009). Selected chemical properties of the seven indicator congeners are shown in Table 1.1.

PCBs have relatively low vapour pressure, and are therefore categorised as SVOCs (semi-volatile organic compounds). SVOCs present in air partitions between a) pure gas phase b) condensate to particles present in the air/settled dust and c) adsorbs to material surfaces and can be absorbed by the material according to the physical properties of PCBs (Weshler and Nazaroff, 2008). PCBs containing a low number of chlorine per molecule tend to be more volatile, whereas higher chlorinated congeners are less volatile. For this reason lower chlorinated PCBs typically dominate the PCB congener composition in indoor and outdoor air compared with the congeners composition in materials (Kohler et al., 2002, U.S. EPA, 2011; Carpenter, 2015).

Table 1.1 Chemical properties of the 7 indicator congeners

PCB -#	28	52	101	118	138	153	180
Chemical structure							
Molecular weight, g/mol	257.5	292.0	326.4	326.4	360.9	360.9	395.3
Melting point, °C	59	87	79	113	80	104	114
Boiling point, °C	343.2	362.8	398.8	420.4	425.6	431.6	441.6
Vapour pressure, Pa [a]	$3.41 \cdot 10^{-2}$	$1.61 \cdot 10^{-2}$	$3.39 \cdot 10^{-3}$	$1.19 \cdot 10^{-3}$	$5.14 \cdot 10^{-4}$	$6.83 \cdot 10^{-4}$	$1.41 \cdot 10^{-4}$
Enthalpy of Evaporation, KJ/(K·mol) [b]	78.0	80.8	86.4	89.3	91.9	91.4	96.6
Log K_{oa} [c]	8.09	8.62	9.51	10.0	10.5	10.4	11.3
Diffusion coefficient, ($x10^5$) cm^2/s [d]	5400	5200	5000	5000	4800	4800	-

a Saturated liquid vapour pressures at 25 °C b Enthalpy of evaporation of sub-cooled liquid (Falconer and Bidleman, 1994)
c Koa, partitioning coefficient of octanol and air at 25 °C (Weschler and Nazaroff, 2010)
d Diffusion coefficient in air based on the number of chlorines at 25 °C (Bopp, 1983)

Saturated vapour pressures of subcooled liquid PCBs increase with increasing temperature (Falconer and Bidleman, 1994):

$$\log P_L^\circ = \frac{m_l}{T} + b_l \quad (1)$$

Where P_L° (Pa) is saturated vapour pressure at the temperature T (Kelvin), the constants m_l and b_l represent the slope and intercept unique to each PCB congener taken from Falconer and Bidleman (1994). The constant $m_l = -\Delta H/R$, where ΔH is the enthalpy of evaporation of liquid PCB, which can be assumed constant in the studied temperature range (i.e. well below the boiling point) and R = 8.314 J/(K·mol) is the gas constant (Halsall et al. 1999). Therefore temperature changes affect the volatility of the PCBs (Halsall et al., 1999).

2.3 PCB production, use and release to the environment

Global production and consumption peaked around 1970, and the majority was produced and consumed in the 1960s and early 1970s (Breivik et al., 2002). Due to PCBs physical-chemical properties it had widespread usages and various products such as transformers, capacitors, fluorescent light ballasts, hydraulic fluids, paints, floor materials, ceiling tiles, glue of double-glazed windows, caulks (joint sealants) and other adhesives (Namieśnik et al., 1992; Fromme et al., 1996; Bergsdal et al., 2014). Estimates on the total global production from 1.3-1.7 mio tonnes have been reported in literature (de Voogt and Brinkman, 1989; Breivik et al., 2002; Stockholm Convention on Persistent Organic Pollutants, 2008).

Figure 2.3 Danish fluorescent light ballasts with a PCB congener composition similar to Aroclor 1248.

PCBs were not produced in Denmark, but PCBs were imported from other countries i.e. Germany. It is estimated that 1100-2000 tonnes of PCB have been used in Denmark in products such as capacitors among others light ballast, transformers,

paints, sealant and glue (DK EPA, 1983). Figure 2.3 shows a Photo of two fluorescent light ballasts dismounted in 2014 in a Danish elementary school.

In 1966, Scientist Søren Jensen reported the discovery of environmental occurrence of PCBs (Jensen, 1966). Hereafter scientists began to worry about tentative signs of omnipresence and bioaccumulation of PCBs (Risebrough and Brodine, 1970; Jensen, 1972; WHO, 1975). PCBs are detectible in very different compartments of the environment (Risebrough et al., 1968; Risebrough and Brodine, 1970; Kalmaz and Kalmaz, 1979) and detection of PCBs in as remote areas as the arctic demonstrates the long-range atmospheric transport of PCBs (Oehme and Mano, 1984; Oehme, 1991; Harner et al., 1998; AMAP, 2004)

Today PCBs are known as ubiquitous and persistent environmental pollutants (POP) and considered as a global environmental problem with a well-known potential toxicity, which were included at the 1998 The United Nations Economic Commission for Europe (UN ECE) POP protocol, which objective is to eliminate any discharges and emissions of the selected POPs by scheduled elimination of among others PCBs (UN ECE, 2015).

Within the last 10 years the congener (PCB-11), which have not been produced as part of conventional PCB-mixtures, was detected in air samples in Chicago, Philadelphia and several other sites (Hu et al., 2008). These identifications lead to further research which recognises the unintentional production of PCBs during the synthesis of some pigments that are widely used to colour paints (Hu and Hornbuckle, 2010).

2.4 Human exposure to PCBs

PCBs are traceable in almost every human studied (Longnecker et al., 2003). The primary exposure route for the general population is dietary intake (fatty fish, meat and dairy products) although this has declined over the last decades due to the final bans in 1980s (Nichols et al., 2007; Jensen, 2013). For some people the main exposure route of certain PCBs is the inhalation and dermal uptake from air e.g. occupants of contaminated buildings, proximity to the surrounding environment of waste sites and people exposed though their work (Gabrio et al., 2000; Johansson et al., 2003; Kontsas et al., 2004; Wingfors et al., 2006; Rudel et al., 2008; Meyer et al., 2013; Carpenter, 2015). A further potential exposure risk is ingestion of dust from contaminated buildings (Harrad et al., 2009; Knobeloch et al., 2012). Dermal uptake of PCBs could be substantial from air and though skin contact with indoor surfaces, dust and clothing as seen for other SVOCs (Morrison et al., 2014; Weschler and Nazaroff, 2014). Furthermore PCBs are passed from mother to child during pregnancy and breastfeeding (Higuchi, 1976; Yakushiji et al., 1984; Jacobson et al., 1990).

Highly chlorinated PCBs are more resistant to degradation than lower chlorinated PCBs and therefore bioaccumulate to a larger extent and have longer half-lives in the environment as well as in the human body (Robertson and Hansen, 2001). The distribution of PCB congeners (the congener pattern) in an exposed individual can reveal the route of exposure e.g. prevalence of low-chlorinated congeners is associated with inhalation-exposure whereas often the higher chlorinated congeners predominate following dietary exposure (Ampleman et al., 2015). The exposure through inhalation can be significant in contaminated buildings. Meyer et al. (2013) showed a correlation between levels of the lower chlorinated PCBs (3-5 chlorine) in indoor air and plasma levels of the residents and in addition the plasma content correlated with the exposure duration in contaminated flats. For PCB-28 the plasma levels were found to be 100 times higher in an exposed group compared with a reference group in the same housing estate (Meyer et al. 2013). Fitzgerald et al. (2011) found the serum concentration of PCB-28 and PCB-105 associated with indoor air concentration, even at low indoor air concentrations (<10 ng/m^3), however exposure duration is relatively long with a mean of 33 years.

2.5 Health effects of PCBs

During the 1930s and 40s occupational exposure to high concentration fumes of PCBs resulted in dermatologic effects as chloracne, disturbances of the digestive system, impotence, and even fatal cases has been reported (Jones and Alden, 1936; Drinker et al., 1937; Greenburg et al., 1939; Miller, 1944; Jensen, 2013).

In 1968, a major accidental food contamination of rice oil named Yusho (oil disease in Japanese) occurred in Japan, poisoning more than 1800 people (Yoshimura, 2003). Eleven years later a similar contamination named Yu-cheng (oil disease in Taiwan) occurred in Taiwan, this time poisoning more than 2000 people (Hsu et al., 1994). These two major poisoning accidents include not only PCBs but also various other dioxins-like compounds such as polychlorinated dibenzofurans (Rappe et al., 1979; Chen et al., 1984). The poisoning caused different symptoms and health effects such as pigmentations of nails, skin and mucous membrane, chloracne, palm sweating, itching, swelling of eyelids and limbs, eye discharge, headache, fever, visual and hearing disturbances (Higuchi, 1976). The babies of pregnant woman during the accidents and kids born later of mothers who were exposed under the accidents have higher risk of being stillborn, nail deformity, dark-brown pigmentation of skin, tooth and bone defects, temporally suppressed growth and decreased cognitive performance and other risks (Higuchi 1976; Yoshimra and Ikeda, 1978; Lai et al., 1994). Since the two food poisoning incidents include not only PCBs conclusions on health effects from PCBs contamination are difficult. Comparison between occupational exposure effects and clinical reports of the food poisoning show less severe effects of occupational exposure. This was even at high dose exposure (assessed by high blood levels) compared with the poison accidents.

An explanation for the lower effect of occupational exposure could be the Healthy Worker Effect (Shah, 2009), where use of healthy workers in epidemiology studies is biased compared with the general population due to the general improved health status of workers. Nevertheless signs of chloracne, pigmentation changes and changes in the lever are reported in both cases (Ikeda, 1996).

Over the years it has become clear that the individual PCB congeners have different health effects on humans and animals. The PCBs are divided in two groups according to their toxic mechanism of action: dioxin-like and non-dioxin-like PCBs. 12 PCB congeners exert dioxin-like biological and toxic effects and are denoted dioxin-like PCBs. The two phenyls rings in the PCB molecule rotate relative to each other and for dioxin-like PCBs the two phenyls rings can form a planar conformation (coplanar). This characteristic makes it possible for dioxin-like PCBs to bind to and activate the cytosolic aryl hydrocarbon receptor (AhR) due to their low steric barrier for a planar conformation. This is possible for 12 of the non- and mono-*ortho*-PCBs; meaning none or at maximum one chlorine is positioned at 2, 2´, 6 and 6´ in Figure 2.1. Four of them (non-*ortho*-PCBs) have strong affinity for the AhR whereas the remaining eight dioxin-like PCBs (mono-*ortho*-PCBs) bind weakly to the AhR (Erikson and Kaley 2011). The four non-*ortho*-PCBs are by WHO considered between 3.3 (PCB-77) and 3,333 times (PCB-126) more toxic in dioxin-like properties than the eight mono-*ortho*-PCBs (Van den Berg et al., 2006).

The International Agency for Research on Cancer *IARC* categorised all PCB congeners as Group 1 carcinogenic to humans in 2013 (Lauby-Secretan et al., 2013; IARC Monographs, 2015). The known types of cancers in humans and experimental animals include malignant melanoma, cancer in oral mucosa as well as thyroid, pancreatic, stomach, lung, liver and brain cancer (Robertson and Hansen, 2001; Jensen, 2013; Lauby-Secretan et al., 2013). Clear associations with breast cancer risk are demonstrated in a study of PCBs measured in breast adipose tissue (Aronson et al., 2000). Additionally increased risk of childhood leukaemia is associated with PCB content in carpet dust in Ward et al. (2009).

Exposure to PCBs is also known to cause higher risk of adverse immunological, reproductive, and dermatological effects. PCBs also increase the risk of obesity and type-2 diabetes and affect the cardiac system (Carpenter 1998; Faroon et al., 2003; Jensen 2013). PCBs are known to affect the neuropsychological function and to be the cause of poorer cognitive development (Ribas-Fitó et al., 2001; Walkowiak et al., 2001). Background PCB exposure of foetuses and children pose a critical period regarding developmental health effects (Quinete et al., 2014; Faroon and Ruiz 2015).

Higher chlorinated PCBs have been assumed to pose a higher health risk compared with lower chlorinated PCBs. Recently exposure to the more volatile PCBs present in air and associated with inhalation is found associated with increased risk of

diabetes, hypertension, cardiovascular disease e.g. heart attack, strokes for residents near large PCB waste sides, which indicates how exposure to lower chlorinated PCBs is important from a health perspective (Carpenter, 2015).

2.6 PCB legislation

The increasing health and environmental concern led to extensive legislation on PCBs in many countries during the 1970s. In 1973, OECD and WHO recommended control and phase-out of PCBs (DK EPA 1974; WHO, 1975). In the U.S., the Toxic Substances Control Act (TSCA) of 1976 banned production, distribution, and so-called open application uses of PCBs (TSCA, 1976). The so-called open application is opposed to enclosed uses in electric equipment and hydraulic systems where PCB oils are encapsulated in metal. In most OECD countries including Denmark production, import and usage of PCBs was banned in 1977, except from enclosed uses (DK BEK, 1976a; DK BEK, 1976b). In 1986, a total ban of import and sale of PCBs regardless of their application was passed in Denmark (DK BEK, 1986).

PCBs are among the 12 Persistent Organic Pollutants (POPs) often called the *dirty dozen* listed on the Stockholm Convention from 2001. Most countries including Denmark have committed to the provisions in the Stockholm Convention, which came into force in 2004. The convention provisions require countries to ban production, import and use as well as ensure that PCB stockpiles and waste with PCBs are managed safely and in an environmentally sound manner (Stockholm Convention, 2015). The interpretation of managing PCB stockpiles differs between countries. In Sweden building owners of buildings erected or renovated in the PCB period (1950s-1970s) are required to remove materials such as caulks with PCB concentration above 500 ppm (SFS, 2007).

Denmark has as required by the Stockholm Convention regulation on waste management, but no such regulation on removal of PCB-containing building materials. In 2009, Danish National Board of Health issued guideline action levels on concentrations of PCB-total in indoor air (DK NBH, 2011; DK MEB, 2011). The air concentration of PCB_{total} is determined as PCB_{sum7} times a factor of five.

Guideline action values for PCB indoor air concentrations:

< 300 ng/m³	Considered without health risk
300-3000 ng/m³	long-term exposure is assumed harmful to health and action to reduce concentration is advised
> 3000 ng/m³	immediate action to reduce concentration is advised due to the considered increased health risk

The Danish guideline values are based on a German measure for the Tolerable Daily Intake (TDI) of PCBs. The exposure through inhalation of air with a concentration of 300 ng/m³ corresponds to 10% of TDI, whereas 3000 ng/m³ corresponds to 100% for adults (Benthe et al., 1992). In United States, EPA have established public health guidance specific to the type of environment according to age of occupants, assumed behaviours, body weights of the pupils and time in school (U.S. EPA, 2012d; U.S. EPA, 2015). These considerations are not taken into account in Denmark. However the Danish Working Environment Authority consider the reduced occupational occupancy of buildings due to limited working hours and allows PCB-total air concentrations up to 1,200 ng/m³ in working environments, with occupancy of 37 hours/week and accordingly higher concentration when occupancy is shorter (DK WEA, 2001).

2.7 PCB in buildings

PCBs have been identified in building materials in different countries such as Australia, Canada, Denmark, Finland, Germany, Japan, New Zealand, Norway, Sweden, Switzerland, United Kingdom and United States, which in many cases have been documented to result in elevated indoor air levels due to PCB containing caulks (Balfanz et al., 1993; Fromme et al., 1996; Bleeker et al., 1999; Sundahl et al., 1999; Coghlan et al., 2002; Corner et al., 2002; Kohler et al., 2002; Herrick et al., 2004; Hosomi, 2005; Priha et al., 2005; Heinzow et al., 2007; Harrad et al., 2009; Frederiksen et al., 2012; Bergsdal et al., 2014).

PCBs in caulks are believed to have been used from 1950 until it was banned; paints might have been produced even earlier (Scott and Snyder, 2015). PCBs were added to the caulks as plasticiser and typically the caulks have been used around windows and/or as joints between concrete elements (Figure 2.4). In some cases caulks are visual from inside (interior), in other cases the caulks are exterior used for sealing of the building envelope, and finally some buildings have both interior and exterior caulks. PCBs spread from buildings to the surrounding environment; both to ambient air and surrounding soil (Halsall et al., 1995; Andersson et al.,

2004; Herrick et al., 2007). The concentration of PCBs in soil decreases with the distance to the building (Priha et al., 2005).

Figure 2.4 PCB containing caulk between interior concrete wall elements in a Danish elementary school.

In 2000, the organization of sealant branch's manufacturers and distributors estimated that 75 tons PCB was still present in building caulks in Denmark (Wilkens et al., 2002). Gunnarsen et al. (2009) estimated the remaining amount of PCBs in caulks to be 6-21 tons. In 2013, the Danish Energy Agency published the report of the national investigation of the occurrence of PCB in material and indoor air in Danish Buildings erected in the period 1950-1977. The number and different types of buildings are selected on the basis of a statistical analysis of the building stock. Approx. 75% of the investigated buildings had PCB containing materials with a concentration over 0.1 mg/kg. In the report the remaining amount of PCBs in caulks is estimated to be 9-50 tons and 17-87 tons in building materials in general (Danish Energy Agency, 2013a). The national survey also resulted in an estimate that 0.7-1.5% of all Danish buildings (incl. buildings erected before and after the PCB period) have concentrations of PCBs in indoor above the Danish action level of 300 ng/m³ (Danish Energy Agency, 2013a). The investigation found public schools to have high prevalence for PCB concentrations in indoor air exceeding the Danish action level compared with other public buildings (Danish Energy Agency, 2013b).

2.7.1 Primary, secondary and tertiary PCB sources

The PCB-sources that were originally introduces to the buildings either as paints, light-ballasts, caulks or other PCB products are known in literature as *primary sources* (U.S. EPA, 2012a). Other materials in direct contact with primary source materials can get contaminated by diffusion of PCBs from the primary sources to the adjoining materials. These materials will eventually constitute a source of PCB

and are known as *secondary sources* (U.S. EPA, 2012a). In addition, PCBs does not only migrate to adjacent materials, they also evaporate into the air and subsequently contaminate interior surfaces through ad- and absorption of air borne PBCs. These large interior surface sources contaminated by air are defined as *tertiary sources* in Kolarik et al. (2014a). However, in most literature on PCBs in buildings tertiary sources and secondary sources are not distinguished and contaminated materials other than primary sources are characterised as secondary sources.

Figure 2.5 schematically shows the spread of PCBs indoors from PCB containing caulk (primary sources) around a window to adjacent materials (secondary sources), indoor air and indoor surfaces (tertiary sources). The secondary sources and the tertiary contaminated surfaces have the ability to re-emit PCBs to the air (U.S. EPA 2012a). These sources are capable of sustaining considerable indoor concentrations even after the primary sources are removed (Benthe et al., 1992; Weshler and Nazaroff, 2008).

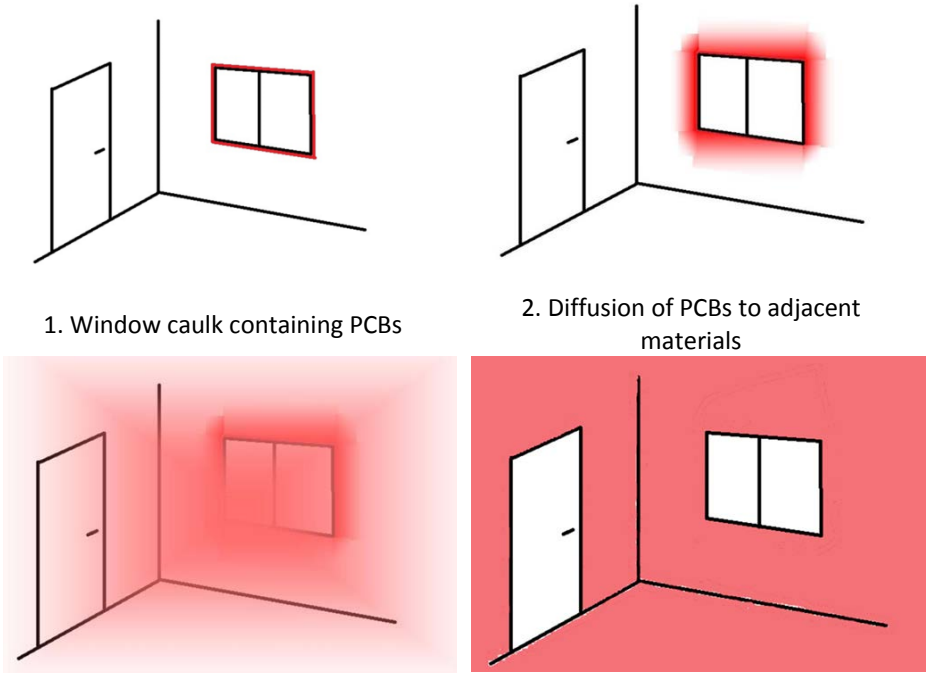


Figure 2.5 Schematic figures of transport mechanisms of PCBs indoors over time.

2.7.2 PCBs in indoor air

The air concentration varies from building to building as well as room to room and the variation is caused by source characteristics such as the physicochemical properties of the source, concentration of PCB in the source, amount, size, location and source strength. The congener pattern (composition of the individual congeners) in the source affects the congener pattern in the air (Heinzow et al., 2007). However, since the lower chlorinated PCBs evaporate more easily, the congener pattern in the air concentration is shifted towards the lower chlorinated PCBs compared with the sources (Benthe et al., 1992; Sundahl et al., 1999; Kohler et al., 2002; U.S. EPA, 2011). In addition to the varying air concentrations due to differences in sources and physical building characteristics several other variables such as air exchange rate and temperature affect the PCB concentration in indoor air.

The air exchange rate is known to affect the air concentration (MacIntosh et al., 2012). In Massachusetts, a PCB contaminated elementary school had different selected engineering controls implemented in order to lower the PCB indoor air concentrations. Increased ventilation, being one of the mitigation methods, significantly lowered the PCB concentration on average from 423 to 173 ng/m³ (MacIntosh et al., 2012), though the particular air exchange rate (ACH) is not available for the respective rooms. Nor was the effect of ventilation on highly contaminated rooms investigated in the study by MacIntosh et al. (2012).

The air exchange rate has an influence on the concentration or the emission rate of compounds in the air giving the mass balance, and assuming clean outside air, no sorption and the only removal of mass provided by the ventilation. The steady-state air concentration, C_g (µg/m^3) in a defined volume, V (m^3) with an ACH, n (h^{-1}) is correlated with the total emission rate, E (µg/h) as follows:

$$C_g = E/(n \cdot V) \quad (2)$$

If the total emission rate, of PCBs to the indoor air is constant then the air exchange rate will dilute the concentration by half when the air exchange rate is doubled. This is not necessarily the case for PCB, since PCB-emission rates are subject to external boundary layer control mechanisms like the convective mass transfer coefficient, as is the case for SVOCs.

A boundary layer exists between the source surface and the main flow as air passes over the material surface (Huang and Haghighat, 2002; Liu et al., 2014). The PCB mass transfer in this boundary layer is determined by diffusion and convection (Sissom and Pitts, 1972). The source emission, *E* (µg/s), can be described by the following equation:

$$\mathrm{E} = h_m A_{SO}\left(C_{ai} - C_g\right) \quad (3)$$

Where h_m (m/s) represent the mass transfer coefficient, A_{SO} is the source area (m^2), C_{ai} (µg /m^3) the air concentration immediately adjacent to the source surface and C_g (µg/m^3) the gas phase concentration in bulk air. The emission rate is assumed not to be limited by diffusion within the emitting material. An increase in ventilation seeks to dilute the gas-phase concentration C_g, and thereby the concentration gradient ($C_{ai} - C_g$), may increase and eventually enhancing the emission. Increased ventilation may also cause increased air velocity, *u* (m/s), close to the source surface, thereby increasing the mass transfer coefficient with $u^{1/2}$ for laminar flow and $u^{4/5}$ for turbulent flow (Huang and Hagighat, 2002).

The boundary layer close to surfaces is defined as the area where air velocities are affected by non-negligible viscous forces and within this layer the air velocities varies from zero at the surface to the bulk air velocity. The convective mass transfer, h_m, can theoretically be expressed as:

$$h_m = \frac{D_g}{\delta} \quad (4)$$

Where D_g (m^2/s) is diffusion coefficient of PCBs in air and δ (m) is the boundary layer thickness (Sissom and Pitts, 1972).

Other parameters are known to have an impact on the indoor air concentrations of PCB. Unpublished measurements of indoor air concentration measured in Denmark were found to be increased on the windward side of the building compared with the lee side in a building with exterior caulks. Benthe et al. (1992) also found wind impact to influence PCB concentrations in air.

Increased temperature is known to increase air concentration; Bent et al. (2000) measured PCB air concentrations, indoor temperature and outdoor temperature regularly in a room. Increased in- and outdoor temperature was found to cause a multiple increase in the PCB air concentrations. In Kohler et al. (2005) indoor temperature was recognized as a driving parameter for increased PCB air concentrations in 112 rooms from different buildings. Balfanz et al. (1993) measured air concentrations in 10 rooms with exterior PCB caulks during summer and wither at comparable indoor temperatures, and found significantly higher concentrations during summer compared with winter. Benthe et al. (1992) additionally concludes outdoor temperature to affect indoor concentrations.

Outdoor air concentrations of PCBs were found strongly dependent on temperature at one location during a stable meteorological period, suggesting that equilibrium between atmosphere and surface was achieved as a function of either vapour pressure or the octanol-air partitioning coefficient (Halsall et al. 1999).

In a chamber study of PCB emissions from one caulk sample, a log-linear correlation was found between the vapour pressure of the congener and the emission rate of the congener (Guo et al. 2011). Since vapour pressures change with temperature (Falconer and Bidleman, 1994) consequently emission rate is affected by the temperature. However few studies have thoroughly investigated the influence of temperature on PCB air concentration in full scale contaminated buildings.

Both the effect of indoor temperature and ventilation on air concentrations is investigated thoroughly in this current thesis.

2.8 Remediation of PCBs in buildings

Unacceptable levels of PCB in the indoor air lead to a need for remediation. Renovation or demolition of buildings with PCB requires special demands in handling the construction waste containing PCB (DK BEK, 2012). Further, protection of the surrounding environment, workers and occupants has to be taken into account. Renovation, demolition and in some cases remediation of buildings with PCB creates construction waste, which needs to be categorized and separated in waste classes from recycling to hazardous waste in accordance with current legislation (DK BEK, 2012). Furthermore, remediation of buildings with contaminated air can be a challenging task, among other things because simple removal of primary sources has shown insufficient in solving the problem (Benthe et al., 1992; Weshler and Nazaroff, 2008).

In order to reduce indoor exposure via air and meet guideline action values several remediation measures can be necessary (Benthe et al., 1992; Bent et al., 1994; Bent et al., 2000; Chang et al., 2002; MacIntosh et al., 2012; U.S. EPA, 2012d; SBi, 2013). One method to reduce occupant exposure is by reducing emissions rates. Emission can be reduced by *abatement* measures defined as physical removal or chemical modification of the source. M*itigation* measures where the exposure impact are reduced by engineering controls include methods such as encapsulation of the emission, increased ventilation, temperature control, and restricted occupancy of the building (VDI, 2009; U.S. EPA, 2012b; U.S. EPA, 2012c; U.S. EPA, 2012d; SBi, 2013b; Kolarik, 2014b; Frederiksen et al., 2015).

Abatement measures include:

- Removal of building materials in general such as ceiling tiles, floor materials and light ballasts
- Removal of caulks and cutting out adjacent materials
- Removal of paint and other finishes by blasting with sand, glass bead, Sponge-jet, metal shot, high pressure water or dry ice.
- Removal of layers of concrete by scarification, scabblers, grinders or roto-peening
- Chemical extraction of PCB with different adsorbent materials
- Chemical modification of the source such as dechlorination by AMTS
- Thermal stripping where the building or materials is excessively heated (50-60 °C) for days to weeks in order to accelerate evaporation of PCBs under high air change rate with air cleaning using activated carbon filters, after primary sources and heat sensitive materials have been removed

Mitigation measures include:

- Encapsulation of emission with different materials such as adhesive aluminium foil, epoxy, Acrylic products and others
- Ventilation
- Air cleaning
- Decreasing indoor temperature and/or installation of solar shading
- Increased and thorough cleaning
- Limited use of the contaminated rooms or buildings

The mitigation methods are often interim and recommended as a first action when an unacceptable indoor air concentration is found. In some cases mitigation measures like increased ventilation and temperature control is sufficient for obtaining acceptable air concentration levels, though in others cases several and intrusive abatement measured are required. Further studies on the efficiency of abatement and mitigating measures are needed. This includes investigation of the effect of temperature and ventilation.

There is a need for development of inexpensive methods to estimate the necessary remediation required to reduce air concentrations to an acceptable level. It can be difficult to know beforehand which measures are sufficient. How severe is the contamination; will it be enough to remove the primary sources? Is it necessary to remove the adjacent materials of the primary sources? What about the rest of

indoor surfaces of the building? What is the emission potential of the sources? Is it possible to encapsulate the sources and are the sources suitable for encapsulation. And if so what encapsulation material is best suited for the purpose? Therefore, there is a need to characterise PCB sources, by measuring emission rates of PCBs from these sources, in order to prioritise means of mitigation.

Different small-scale climate/environmental/emission test chambers have been used to measure emissions rates for different compounds from building materials and require destructive cutting out of building materials (U.S. EPA, 2011; Xu et al. 2012; Liu et al. 2013). Other chambers differ from regular cubic and rectangular cuboid small-scale chambers by having one open side, and the planar building material (source) constitutes a part of the chamber enclosure during measurements. This type of chambers is called *Emission Test Cell* (ISO, 2006). In this study an emission test cell for in situ emission measurement were developed and used to measure emissions from various surfaces. ISO (2006) lists a number of different requirements for an emission test cell including the following requirements which was fulfilled by the developed emission test cell; non-absorbing materials such as glass or stainless steel, low absorbing and emitting sealing materials, air tight, clean inlet air and sampling flow below 90% of inlet flow. The design of the developed emission test cell is described in section 3.1.3.

3 Methodology

This chapter describes the general methodology of the research conducted to test the hypotheses. The study design, the measuring procedure and the statistical analyses used are summarized. Further detailed information can be found in the descriptions given in Paper I-IV.

3.1 Study design

3.1.1 Ventilation

The effect of ventilation on PCB concentrations in indoor air was investigated by two different approaches. The first approach was collecting and reviewing existing cases with concentration measurements at different ACHs. Inclusion criterion was met if PCB concentration in indoor air was measured at least twice in the same room; with and without mechanical ventilation in operation or before and after a known change in the ventilation rate. Client consultants, working with mitigation of PCB-contaminated buildings, and some municipalities with known PCB-contaminated municipal buildings, were contacted and they identified and provided cases with relevant data. Nine buildings with a total of 30 rooms that had relevant measurements of PCB concentration in indoor air were identified.

The second approach to study the effect of ventilation was done by two different intervention studies. In the intervention studies mechanical ventilation was installed in three highly contaminated rooms and the concentrations of PCB in the air as well as air change rate (ACH) and temperature were measured. In the first room (classroom) the test was conducted without mechanical ventilation (ACH = 0.2 h^{-1}) and with mechanical ventilation (ACH = 5.5 h^{-1}). In the other two rooms (bedrooms), the effect of four different ACHs (0.5, 2.2, 4.5 and 6.6 h^{-1}) was investigated (Paper II).

Temperature has a strong influence on vapour pressure of PCBs and is an important parameter influencing the air concentrations, therefore temperature was measured during the air sampling and the PCB concentrations were adjusted to the chosen reference temperature of 21 degrees in order to make measurements comparable despite different temperatures during sampling. The adjustment for temperature based on change in vapour pressure (Paper I and II). The method of temperature adjustment is described in section 3.4 as well as Paper I and II. Validation of this temperature adjustment method is given through Paper III and discussed in section 5.2.

3.1.2 Temperature

Since temperature has a significant impact on air concentrations of PCBs, it was decided to study the effect of temperature after the ventilation investigations were completed. This study was also performed to supports the adjustments for temperature of the concentration measurements done in Paper I and II.

In an intervention study the temperature was increased incrementally and steady-state temperatures and the corresponding steady-state concentrations of PCB were measured. Temperature was increased to 20, 22, 25 and 28 °C. The experiment was repeated one year later, changing the temperature from 30 to 24 °C. The Clausius-Clapeyron equation (Eq. 5) was used to model concentrations at different temperatures and model predictions were tested on the intervention measurements (paper III).

Additional field data from a pilot remediation case in one apartment with temperature and air concentrations measured 98 times throughout one year was provided and analysed. The effect of temperature as well as model predictions were tested on these data too (Paper III).

3.1.3 Emission test cell

In order to develop a new tool for in situ measurements of PCB emissions an emission test cell prototype was built of a stainless steel kitchen sink. This was a cheap solution and the sink could easily be mounted on the wall with the open side towards the building surface. The emission test cell was further developed and was eventually made of a stainless steel food pan of the type for use in industrial kitchens. The emission test cell was sealed to the source surface by butyl sealing tape. The supply air in the field tests was filtered indoor air using a commercial air cleaner. The air cleaner was designed to adsorb PCBs with an activate carbon filter. Particle filters inside the air cleaner and after the pump were intended to retain particles from indoor air, the carbon filter and the pump (Figure 3.1).

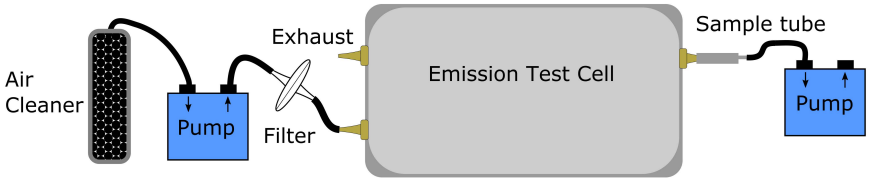


Figure 3.1 Sketch of the emission test cell installation during field measurements.

Connecting tubes were made of silicone, and inlet tubes were wrapped in adhesive aluminium tape to ensure clean inlet air. PCB concentration in the inlet air supplied to the test cell was below detection limit (< 0.5 ng/m³). Inlet flow of 1 l/min was

chosen to match the area-specific ventilation rate of 0.12 l/(s·m²) as in the Nordtest model room with an air change rate of 1 h^{-1} (Nordtest Method, 1998). Sampling flow was approx. 80% of the inlet airflow. A ventilator was installed inside the test cell to ensure well mixed air. The test cell was used to measure emission from different kind of surfaces in situ in two contaminated buildings (Paper IV). In addition, the test cell was used to measure emissions in the laboratory from PCB painted stainless steel plates produced for this purpose (Paper IV).

3.2 The studied buildings

In Paper I, data on air concentrations from nine different PCB contaminated buildings were analysed. All had PCB containing interior and/or exterior caulks as primary sources. The 9 building are sparsely described in Paper I. 2 of the 9 buildings were also used in the ventilation intervention (Paper II), an elementary school and apartment building shown in Figure 3.2.. Table 3.1, provides an overview of the different buildings used for experiments.

Table 3.1 Overview of studied buildings in Paper II to IV.

Paper	Study	Design	Buildings	Type	Building	Room
II	Ventilation intervention	On/Of	Hundested School	Elementary School	Block 6	Classroom 21
		Incredimental increase	Farum Midtpunkt	Apartment building	Apartment (427A)	Bedroom A & B
III	Temperature intervention	Incredimental Change	Brøndby Strand	Apartment building	Apartment 6.8.2	Bedroom
	Additional field data	Temperature and concentration data	Farum Midtpunkt	Apartment building	Apartment (429A)	The entire apartment
IV	Emission measurements	Emission rates from 6 diff. surfaces	Fourfeldt-skolen	Elementary School	Main building, building 4 & 5	Corridor 6.64, office 4.12 & 5.18
		Pairwise emission rates from 3 surfaces	Brøndby Strand	Apartment building	Apartment 6.8.2	Bedroom and corridor

In Paper II, the two buildings had interior and exterior PCB containing caulks that were encapsulated from inside by self-adhesive aluminium foil. No actual removal of PCB sources were attempted at the time of the intervention studies. The vacated buildings had operational central heating and the excising ventilation systems of

the buildings were not in operation during the intervention. Farum Midtpunkt Housing estate is described in detail by Frederiksen et al. (2012) and Kolarik et al. (2014a) and Hundested Elementary School is described in detail in Paper II.

Building 6, *Hundested School*

Intervention in *Classroom 21, Hundested school*

Apartment building, *Farum Midtpunkt*[1]

Intervention in *Room B,* apartment 427, *Farum M.*

Figure 3.2 Photographs of buildings and the ventilation intervention.

The temperature intervention (Paper III) was conducted in a 15-storage apartment building in Brøndby Strand (Figure 3.3). The Building had exterior PCB containing caulks, no remediation measures was conducted and possible comprehensive spillage of PCB on concrete slabs below the wooden floors, as seen in other part of the building. The apartment, which was vacated at the time, had operational central heating, though additional electrical heating was needed to reach the highest temperature levels.

[1] Photographed by Ty Strange

Apartment building, *Brøndby Strand*

Intervention in apartment 6.8.2, *Brøndby Strand*

Figure 3.3 Photographs of the building and the vacated bedroom.

The additional field data (Paper III) were sampled in *Farum Midtpunkt,* apartment 429, a neighbouring apartment of 427 (Figure 3.2). In Farum Midtpunkt the air samplings (n=98) were conducted frequently in a period of one year, during which different remediation measures were carried out. Description of remediation measures and more details are given in Paper III and in the supplementary material of Paper III.

PCB emissions from building material surfaces were measured in the same apartment (Figure 3.4) as used for the temperature intervention (Paper III). The measurement where done in the bedroom and in the apartment corridor.

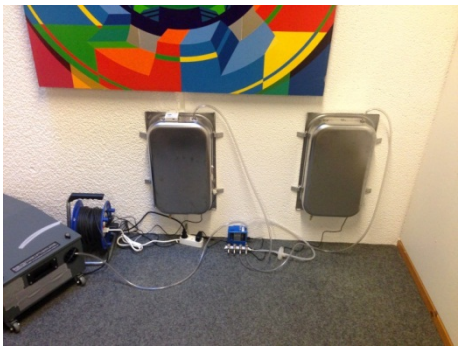
Emission measurements in the bedroom

Emission measurements in the corridor,

Figure 3.4 Photographs of the surface emission measurements in apartment 6.8.2, *Brøndby Strand*.

Additionally, emissions were measured from surfaces in three different rooms in an elementary school, *Fourfeldtskolen* (Figure 3.5). The school has interior and exterior PCB containing caulks, and some of the surfaces in this school had undergone remediation prior to the measurements. Description of this school is provided in Paper IV.

Elementary school, *Fourfeldtskolen*



Surface emission measurements from *Fourfeldtskolen*

Figure 3.5 Photographs of the school and the surface emission measurements.

3.3 PCB sampling and chemical analyses

3.3.1 PCB air sampling

Air concentrations were measured by active air sampling with adsorbent tubes, type: SKC 226-58, with quartz filter, two zones of XAD-2 and PUF (SKC Inc., Eighty Four, PA, US). Sampling flow, time and pump types can be found in Table 3.2. Sampling flow was measured either by a calibrated flowmeter (SHO-rate, model 534-D5-22-VP3, Brooks instruments B.V., The Netherlands) or Gilian Gilibrator-2 (Sensidyne, St. Petersburg, FL, US), a bubble generating flowmeter. Sampling flow rates decreased up to 11%. Sampling of indoor air were done placing adsorbent tubes horizontally approximately 1 m above the floor and adsorbent tubes were fitted with small PTFE nozzles giving an inlet velocity of 1.25 m/s at a flow of 1.9 l/min for collecting suspended dust.

3.3.2 Chemical analyses of adsorbent tubes

In Paper I with the ventilation case reviews the sampling and chemical analyses methods are in most cases unknown and therefore not described.

In the test cell measurements preformed in the laboratory (Paper III), air was sampled using FLEC air pumps (CHEMATEC ApS, Dr. Sofiesvej, Roskilde, DK) with a flow of 0.41 l/min ± 14% for approximately 48 h (range 42-50h). Air samples were analysed in the laboratory for the 12 PCB congeners; PCB-8, PCB-18, PCB-28/32, PCB-44, PCB-49, PCB-52, PCB-66, PCB-70, PCB-101, PCB-118, PCB-138 and PCB-153. Analyses was done by extraction of the adsorbent material with a 1:1 (v/v) mixture of cyclohexane and acetone in an ultrasonic cleaner for 30 min. Prior to the analysis 10 µl of internal standard (PCB Mixture C13 labelled) was added to 90 µl extract. Analysis were performed on GC/MS system, Bruker CP-8400 auto sampler and VF-5MS column, from Agilent Technologies. Quality control efforts included evaluation of recoveries with 4.4'-Dibromooctafluorobiphenyl, adsorbent tube blanks, solvent blanks, duplicate air sampling, and breakthrough investigation. The detection limits are determined between 14 and 32 ng/m³ for 6 PCB congeners; PCB-28, PCB-52, PCB-101, PCB-118, PCB-138 and PCB-153. PCB-28 and PCB-32 could not be separated by the standard column used. Further details on the analyses can be found in the supplementary material of Paper IV.

All other air samples was analysed for the 7 indicator PCBs; PCB-28, PCB-52, PCB-101, PCB-118, PCB-138, PCB-153 and PCB-180. Analyses were performed by the chemical analysis companies listed in table 3.2. Details of the chemical analysis can be found in the respective Papers (II, III and IV) and the associated supplementary materials. The uncertainty of measurements is calculated from the duplicate measurement measured simultaneously at least 1 m apart with the largest difference between them.

Table 3.2 Information on air sampling and chemical analysis companies

	Location	Sampling pumps	Sampling flow/ time	Chemical analysis company	Expanded analytic uncertainty	Detection limit ng/tube	Uncertainty of measure-ments[c]
Paper II Ventilation intervention	Hundested School	GilAir 5[a]	~ 1.9 l/min 21-47 h	Eurofins Denmark A/S	up to ±38%	0.2	<20%
	Farum Apartment 427	GilAir 5[a]	~ 1.9 l/min 23-26 h	Dansk Miljø analyse ApS	±20%	0.5	<22%
Paper III Temperature study	Brøndby Apartment	GilAir 5[a]	~ 1.9 l/min 3.4–14.2 h	Dansk Miljø analyse ApS	±20%	0.5	<14%
	Farum Apartment 429	Buck Elite-5[b]	1-1.9 l/min 3-26 h	ALS Denmark A/S	±20%	0.25	-
Paper IV Emission Test Cell	Fourfeldt School & Brøndby Apartment	GilAir Plus[a]	~ 0.8 l/min ~ 24 h	Eurofins Denmark A/S	up to ±38%	0.2	-

- Unknown
[a] Sensidyne, St. Petersburg, FL, US.
[b] A. P. Buck Inc., Orlando, FL, US.
[C] Uncertainty is calculated from largest difference in duplicate measurements measured simultaneously at least 1 m apart.

3.3.3 Efficiency test of adsorbent tubes

The efficiency of an adsorbent tube depends on the capacity of the adsorbent and the volume of air drawn through the medium. Different efficiency experiments were performed in order to ensure the functionality of the selected type of adsorbent tubes at the given sampling conditions. The efficiency of the sampling tubes was tested according to the chosen sampling durations, temperature conditions and elevated concentrations. The efficiency was tested under worst case conditions in regard to the conditions in this study and by sampling with two sampling tubes in series and separately analysing the two sampling tubes.

Breakthrough experiment 1, were performed at 25˚C with a flow of approx. 1.9 l/min. Sampling duration was 3 days. PCB_{total} concentration in the air was approx. 1500 ng/m³. Breakthrough was only detected for PCB-28 and PCB-52 and was below 1.5% for both congeners.

Breakthrough experiment 2, were performed at 29˚C with a flow of approx. 1.9 l/min. Sampling duration was 14 h. PCB_{total} concentration in the air was approx. 6000 ng/m³. Breakthrough was not identified, since collected PCB mass on the second tube was below the detection limit for each of the congeners (<0.5 ng).

Breakthrough experiment 3, were conducted at extremely elevated concentrations of PCBs. Concentrations of the 12 different PCBs varied between 2000 and 500,000 ng/m³. Concentrations were measured in a laboratory emission test of a painted plate at 50 °C using the so called Field and Laboratory Emission Cell (FLEC) (Wolkoff et al., 1991). Air was sampled by a flow of approx. 450 ml/min for approx. 48 h. Breakthrough was less than 1.5%. Breakthrough percentages in the three experiments are considered within an acceptable range.

3.3.4 Material concentrations of PCB

Sampling of paints, lacquer (wood floor finishes) and other coatings were done by mechanically scraping off an area of 10 × 10 cm^2. Samples of caulk and linoleum flooring were taken by using a utility knife and cutting out small pieces. All material samples were analysed by Dansk Miljøanalyse ApS, where the material samples were divided into small pieces (1 × 1 mm) for homogenisation. 1 g of the homogenized sample was extracted with a 1:1 (v/v) mixture of cyclohexane and acetone in an ultrasonic cleaner for 1 h. PCB surrogate (dibromooctaflouro-biphenyl) was added prior to the extraction. Injection standard (^{13}C-labelled PCB-202) was added to the extract, prior to the analysis on GC/MS system, with auto sampler and DX-XLB column (part no. 122-1232) from Agilent Technologies, Santa Clara, CA, US. Recovery was determined by the PCB surrogate. The expanded analytic uncertainty is given as ±25%. Detection limit is 0.01 mg/kg.

3.4 Temperature

During concentration measurements Indoor air temperatures were continuously logged using Onset HOBO-U12-012-Datalogger (Onset, Bourne, MA, US) or Tinytags Plus (Gemini Data Loggers Ltd, Chichester, West Sussex, UK). In the temperature intervention study (Paper III), surface temperatures were measured before and after each air sampling of PCBs using Brüel & Kjær Indoor Climate Analyzer Type 1213 (Brüel & Kjær Sound & Vibration Measurement A/S, Nærum, DK).

In order to evaluate the effect of ventilation in Paper I and Paper II it was necessary to adjust concentration for the fluctuating indoor temperatures. Mean temperature in the bedrooms were 21 °C during air samplings and all concentrations (individual congeners) reported in Paper I and Paper II were adjusted to 21˚C according to the following simplified relation:

$$\frac{C_{(T)}}{C_{(21^{\circ}C)}} = \frac{P^{\circ}_{L(T)}}{P^{\circ}_{L(21^{\circ}C)}} \qquad (4)$$

Where C_T (ng/m^3) is the measured concentration at the respective measured temperature T (˚C), $C_{(21˚C)}$ is the adjusted concentration at 21˚C, P_L° (Pa) is the theoretical saturated vapour pressure at the measured temperature and 21˚C. The saturated vapour pressures of PCBs at different temperatures are calculated from Eq. (1). In Paper I-III values of heat of evaporation ΔH and consequently values of m_l are taken from (Falconer and Bidleman, 1994).

Modelled values in Paper III are derived directly from Clausius-Clapeyron Equation. The hypothesis is that the concentration, expressed as partial pressures p_i (Pa) in a defined volume indoors, follows Clausius–Clapeyron equation at different temperatures T (K), like it is the case for the saturated vapour pressures:

$$\ln(P_i) = \frac{a_1}{T} + a_0 \quad (5)$$

Where a_1 = -ΔH/R and the constant a_0 is determined by the general concentration level and contains a reference point of temperature and concentration, which will vary from case to case. The enthalpy of evaporation of sub-cooled liquid PCB congeners ΔH is 78.0, 80.8 and 86.4 KJ/(K·mol), respectively, for PCB-28, PCB-52 and PCB-101 calculated from the slopes (m_l) from Falconer and Bidleman (1994). It is assumed that the source concentration is constant during the intervention periods, i.e. the amount of PCB emitted is relatively small compared with the total content in the source, thereby not influencing the source strength.

To predict the concentration at different temperatures by Eq. (5), an estimate of a_0 is required. a_0 can be estimated from a steady-state concentration measurement, P_1 (Pa), at a given temperature, T_1 (K), though using only one measurement makes the prediction vulnerable to variations in the measurement. With more than one pair of measurements of concentration (P) and temperature (T) the regression function of ln(P) versus the inverse temperature, 1/T can be used by choosing a temperature (e.g. the average) to calculate the corresponding concentration. And the chosen temperature and calculated concentration can be used to estimate a_0, thus all measurements have influence on the estimate of a_0.

The adjustment method based on change in saturated vapour pressure used in Paper I and Paper II differs from using Clausius-Clapeyron equation directly on partial pressures of PCBs (Paper III). The concentrations C_T and $C_{(21˚C)}$ in Eq. (4) are not converted to partial pressures (which for Eq. 4 would have resulted in that concentrations were multiplied by the respective temperature (K)). However, when using the same value of enthalpy of evaporation in the two different approaches for an adjustment of a temperature difference of 10 K, the results using the two different methods differ less than 4%, which is considered within the uncertainty of the measurements.

3.5 Air exchange rate, differential pressure and air velocity

During the intervention studies an oscillating fan constantly mixed the air in the room. Air exchange rate (ACH) was measured by dosing CO_2 as tracer gas and measuring the decay over time (ASTM standard E741-11). CO_2 was measured by CO_2 sensor Vaisala GMM20W (Vaisala, Louisville, CO, US) connected to Onset HOBO-U12-012-datalogger (Onset Computer Corporation, Bourne, MA, US). The air exchange measured without mechanical ventilation may be overestimated since infiltration from neighbouring rooms incorrectly may appear as outdoor air exchange. Nevertheless ACH was measured in a low range (0.2-0.5 h^{-1}) without mechanical ventilation. During the intervention with installed mechanical ventilation the differential pressure between the ventilated rooms and neighbouring rooms was measured to ensure balanced pressure ventilation (Testo 6344 Differential Pressure Transmitter, Testo Inc., Sparta, NJ, US).

Air velocities in in the test cell (Paper IV) were measured in 45 evenly distributed points through a perforated wooden plate approx. 2 cm from source and also in 45 points at the bottom of the test cell, using APM 360 Thermo anemometer (Alnor Instrument Company, Skokie, IL, US). Air velocity ranged between 0.1 and 0.9 m/s, and was in average 0.26 m/s. Figure 3.6 shows the measured velocities near the source surface (range: 0.1- 0.6 m/s). Air is supplied at E/D1, exhaust is located at A/B1, the fan is placed at E5, and sampling port is positioned at E/D9 in figure 3.6.

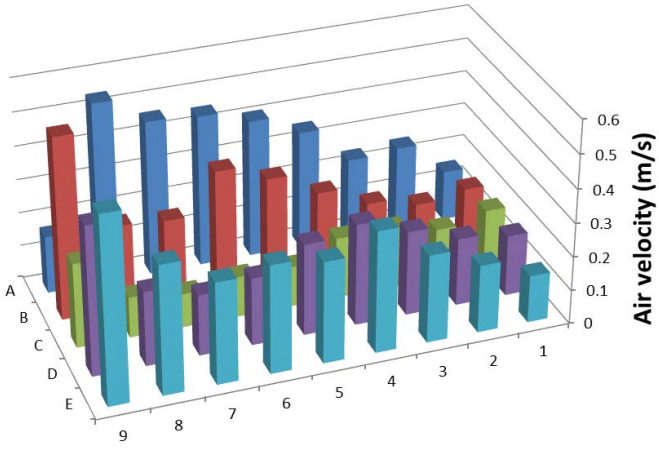


Figure 3.6 Air velocities (m/s) in the test cell near the source surface.

3.6 Statistical analyses

In Paper I, paired-samples t-test was used to determine whether the change in ventilation created a decrease in air concentration using the statistical software SPSS (IBM SPSS Statistics for Windows, Version 22.0., IBM Corp., Armonk, NY, US).

In Paper II and III, all statistical analyses were performed using R software version 3.0.0 (2013-04-03, R Foundation for Statistical Computing, Vienna, Austria). Ventilation data from the classroom were assessed by two sample t-test. Ventilation data from the bedrooms enabled testing the individual effect of ACH and bedroom as well as the interaction of the two by two-way ANOVA and Tukey's HSD. One-way ANOVA and *Tukey's HSD* were used for assessing the difference in mean concentrations measured at the different temperature levels. Simple linear regression was done in Microsoft Excel as well as the calculation of the coefficient of determination, r^2.

The coefficient of determination between measured concentrations and the model (Eq. 6), here distinguished as R^2, was calculated by the equation:

$$R^2 = 1 - \frac{SS_{res}}{SS_{tot}} \quad (6)$$

Where SS_{res} is the residual sum of squares, and SS_{tot} is the total sum of squares.

In Paper IV, statistical analyses were performed using Minitab® 17.2.1 (Minitab, Inc., State College, PA, US). Data were assessed by two-sample t-test, linear and log-linear regression. For all statistical analyses in Paper I-IV the significance threshold was $p < 0.05$.

4 Results

This section gives a summary of the results in the included papers Paper I-IV. Effect of ventilation on PCB concentrations in indoor air is described in Paper I-II. Emissions of PCBs are described in Paper II and the impact of temperature on PCB concentration/emission in indoor air is described in Paper III. The results from the developed test cell measurements are covered by Paper IV.

4.1 The effect of ventilation

The effect of ventilation on PCB concentration indoors was investigated by two different approaches. First existing case data was reviewed (Paper I) and hereafter two intervention studies were carried out with mechanical ventilation where ACHs were controlled (Paper II). All air concentrations in this section are adjusted for temperature according to the method described in section 3.4.

4.1.1 Cases with on/off mechanical ventilation

Figure 4.1, shows concentrations of PCB_{total} measured twice in 26 rooms from 8 different buildings; with and without the mechanical ventilation turned on. In 88% of the rooms, the increased ventilation rates resulted in decreased concentrations, though to varying degrees. In an average concentration decrease 51%, with changes in concentration after an increase in ventilation rate ranging between small increases of up to 150 ng/m^3 and concentrations below detection limit.

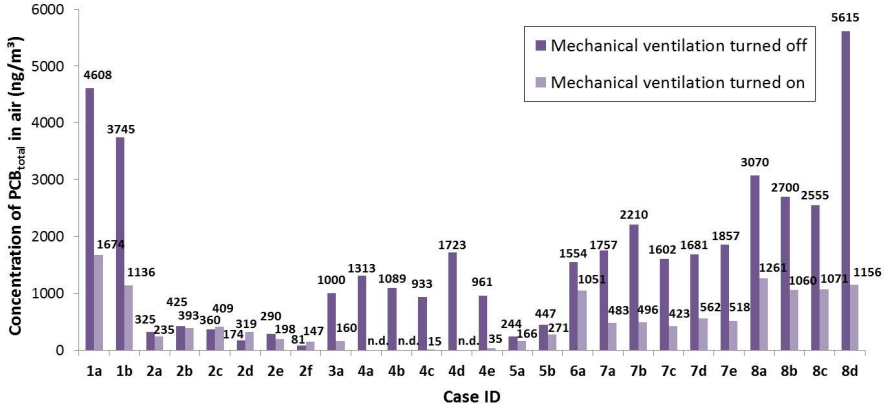


Figure 4.1 PCB_{total} concentrations in indoor air (ng/m³) before and after increasing of the ventilation rate.

In 4 other rooms from 2 different buildings with PCB containing caulks the mechanical ventilation was found to not operate with balanced inlet and outlet

flows (Figure 4.2). Concentrations were measured twice in 2 rooms during conditions with 1) only inlet of air and no mechanical exhaust and 2) balanced increased ventilation. Here concentration increased with balanced increasing ventilation rate. The concentration decreased in the other 2 rooms when the mechanical ventilation consisting of mechanical exhaust was turned off in spite of the lower ventilation rate. These results indicate that differential pressures appear to influence emission rate from PCB containing caulks.

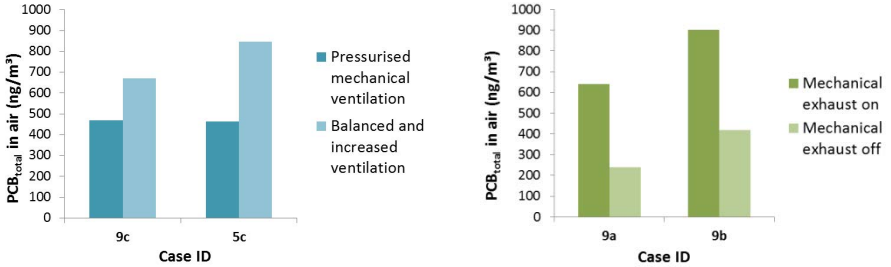


Figure 4.2 PCB_{total} concentrations in indoor air (ng/m³) before and after a change in ventilation rate and a supposed change in differential pressures.

4.1.2 Field intervention studies with mechanical ventilation

In the classroom concentrations were measured without mechanical ventilation (ACH = 0.2 h^{-1}, n=11) and during the intervention with mechanical ventilation (ACH = 5.5 h^{-1}, n=16). Figure 4.3 shows how PCB_{total} only decreased by 30%, even though ventilation rate were increased 27 times, consequently PCB emission increased by more than a factor of 18 (Eq. 2).

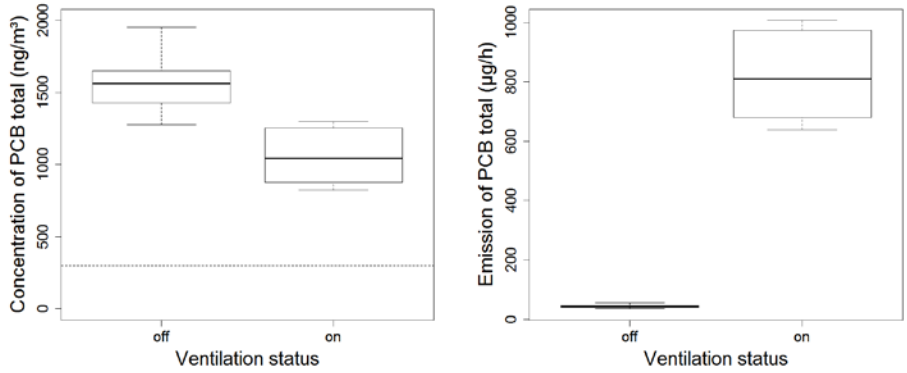


Figure 4.3 Box-whiskers plot of PCB_{total} concentrations in indoor air (ng/m³) and emission rates (µg/h) for ventilation turned off and on in the classroom. The guide-line action level of 300 ng/m^3 is shown by the dashed line in the concentration plot.

The ventilation rate in the 2 bedrooms was increased incrementally from 0.5 to 2.2, 4.5, and 6.6 h^{-1}. Concentrations of PCB_{total} in the bedrooms were lowered at most by 28 and 46%, for Bedroom B and A respectively (Figure 4.4), and the emission rate of PCB was found to increase linearly with increasing air exchange rate (Figure 4.5).

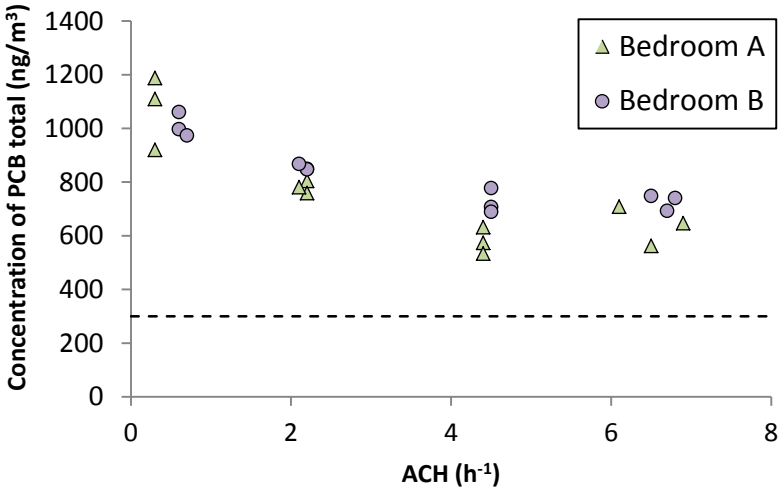


Figure 4.4 PCB_{total} concentrations in indoor air (ng/m³) at different ACH (h^{-1}). The guideline action level of 300 ng/m^3 is shown by the dashed line.

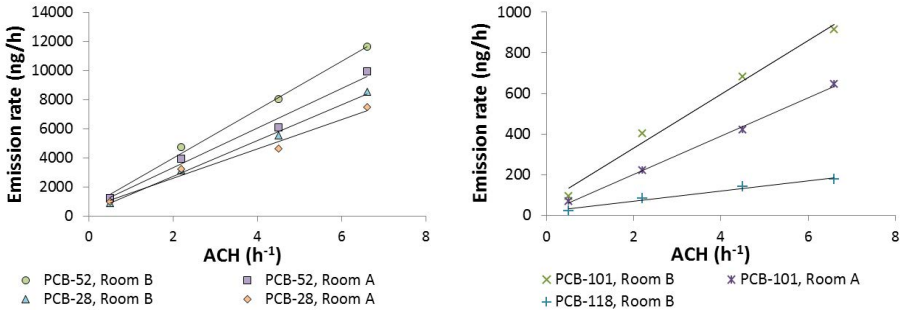


Figure 4.5 Mean emission rates (ng/h) of PCB-28, PCB-52, PCB-101, and PCB-118 at different ACH (h^{-1}) in Bedroom A and B.

4.1.3 Estimation of boundary layer parameters

In the classroom and bedrooms, the PCB-emission rates increased significantly with increasing ACH. The emission rate can be parameterized as a product of mass transfer coefficient, h_m and concentration gradient (Eq.3). Therefore, increased emission rates can relate to changes in both parameters. The boundary layer parameters; h_m and concentration immediately above sources surface, C_{ai} are needed in order to determine to what extent the increase in emission was caused by an increased h_m or an increased gradient between C_{ai} and the bulk air concentration, C_g. However these parameters are not possible to calculate directly based on the ventilation intervention studies.

If there is a linear relationship between the emission rate and C_g, it would mean that h_m was constant, given Eq. 3 where $E = - A \cdot h_m \cdot C_g + A \cdot h_m \cdot C_{ai}$, if assuming C_{ai} to be constant. From Figure 4.6 it is not possible to determine whether the relationship is linear or curved for the three lower ventilation rates. Therefore it was not possible to calculate the parameters h_m and C_{ai} directly based on the ventilation intervention studies.

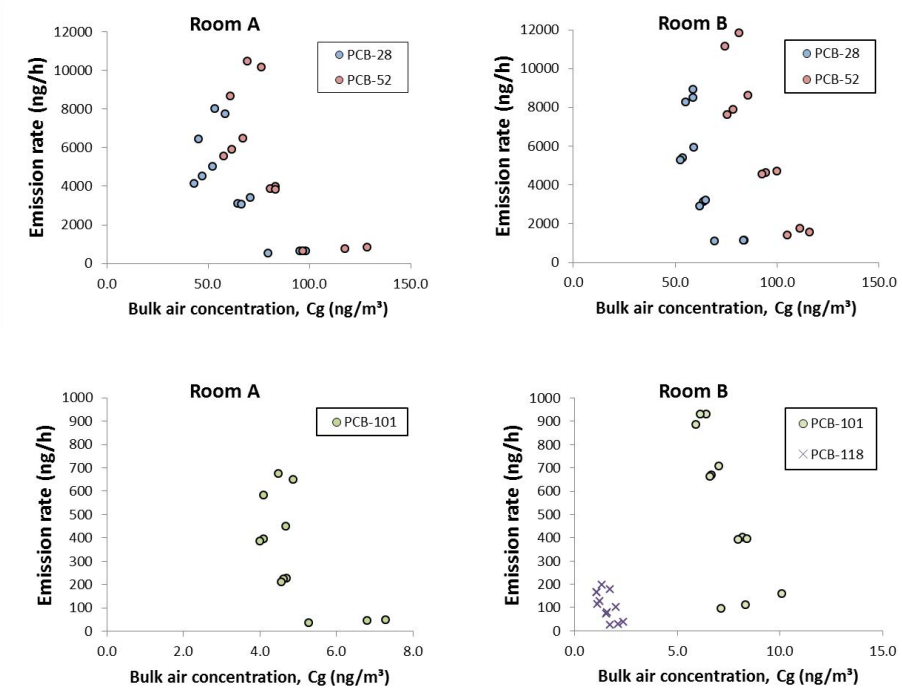


Figure 4.6 Emission rates (ng/h) plotted against bulk air concentration (ng/m³).

In order to get a rough estimate of the impact of increased ventilation of these two parameters mutually, an estimation of C_{ai} is done based on the assumptions that the C_{ai} is constant and the PCB sources in each of the two bedrooms are regarded as one homogeneous source with an area corresponding to the surface area of walls, floor and ceiling of the bedrooms, and that uniform flow regimes exist over bedroom surfaces. In the bedrooms air was supplied directly from a ventilation duct and when ACH is increased consequently higher supply and exhaust airflows are required and higher airflows will result in unchanged or higher air velocities over surfaces in the room. Therefore the convective mass transfer coefficient h_m must be unchanged or increasing for each ventilation level increase for all the detected congeners since h_m is dependent on air velocity. These assumptions was used to estimate C_{ai} and the lowest value of C_{ai} (Eq. 3) fulfilling this requirement for h_m is when assuming C_{ai} at 25% higher that the bulk air concentration, C_g at the lowest ventilation level (no mechanical ventilation, ACH = 0.5 h^{-1}).

The estimations of h_m by assuming this value of C_{ai} for all four ventilation levels are shown in Figure 4.7. The velocity boundary layer thickness, δ can be calculated from h_m and the diffusion coefficient (Eq. 4) and are shown in Figure 4.8 assuming $C_{ai} = 1.25 \cdot C_g$ (0.5 h^{-1}).

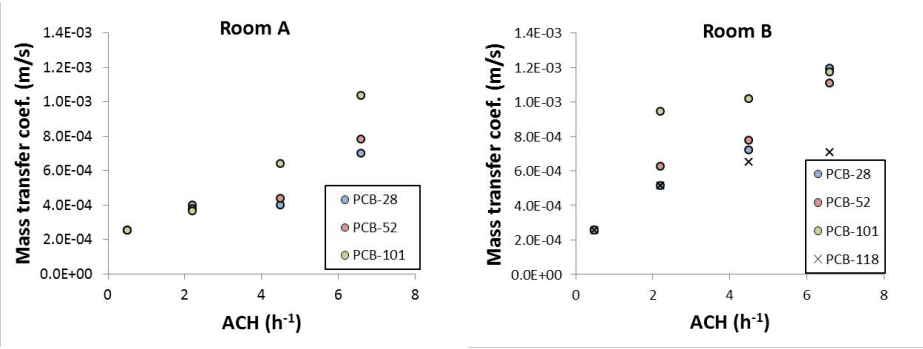


Figure 4.7 Mean convective mass transfer coefficient when assuming C_{ai} to be 25% above C_g at ACH = 0.5 h^{-1}.

The theoretical boundary layer thickness within each level of ACH should not deviate between congeners and since the theoretical boundary layer does not deviate considerably between congeners within each level of ACH the assumption of C_{ai} could be valid.

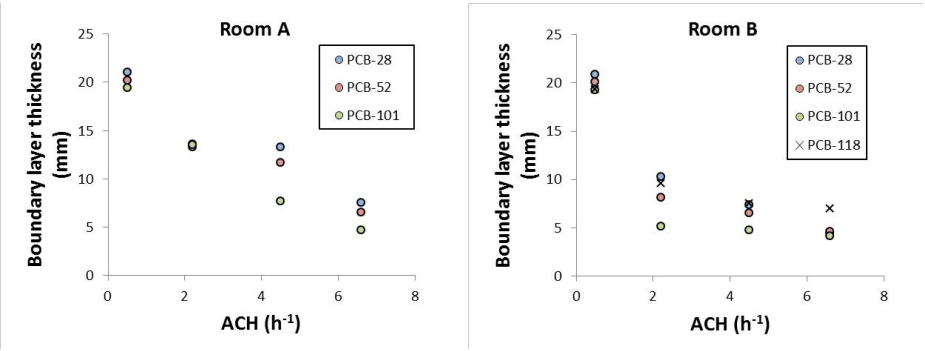


Figure 4.8 Mean boundary layer thickness when assuming C_{ai} to be 25% above C_g at ACH = 0.5 h^{-1}.

The concentration gradient between the concentration immediately above source surface, C_{ai} and the bulk air concentration, C_g is shown in Figure 4.9 also for C_{ai} assumed 25 % above C_g at ACH = 0.5 h^{-1}.

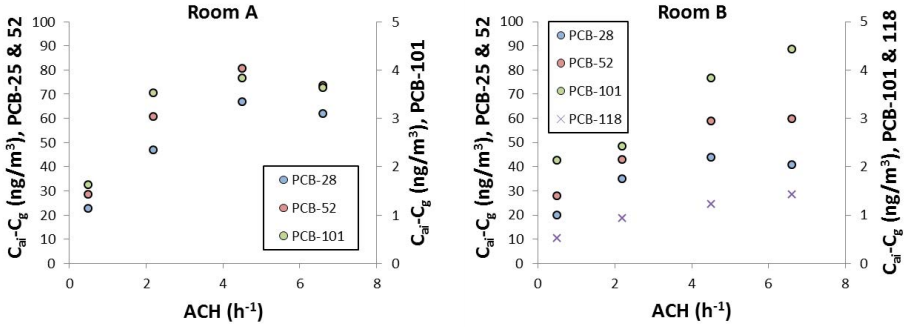


Figure 4.9 Concentration gradient between concentration immediately above the source and the bulk air concentration (C_{ai} - C_g) when assuming C_{ai} to be 25% above C_g at ACH = 0.5 h^{-1}.

Concentration in the classroom was only measured at two different ventilation levels which is an uncertain basis for these speculative calculations, therefore assumptions on boundary layer parameters are not made for the classroom.

4.2 The Impact of temperature

Resembling how the effect of ventilation was investigated by two different approaches, the impact of temperature was also examined by an intervention study and by additional field data from one case apartment (Paper III). Additionally the Clausius- Claperon equation was tested as a method to model the impact of indoor temperatures.

4.2.1 Temperature intervention study

In the intervention study air temperature was changed incrementally to 6 different temperature levels in the following order: 20, 22, 25, 28, 30 and 24 °C. Temperatures levels were retained for min. 3 days before duplicate concentrations were measured once during night time and again the following day. This resulted in 4 measurements for each temperature level. Figure 4.10 shows box-whiskers plot of temperatures in each sampling period.

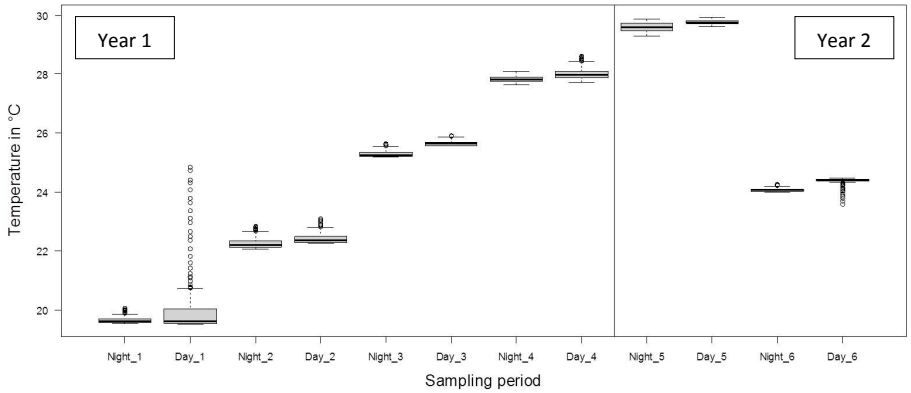


Figure 4.10 Box-whiskers plot of measured temperatures during sampling periods.

PCB-28, PCB-52 and PCB-101 were detectable at all temperature levels and the concentrations were significantly different between different temperature levels (P-value < 0.01). Figure 4.11 shows measured concentrations (ln P) vs. the inverse temperature (1/T) together with the regression lines. Further, the modelled values based on Clausius-Clapeyron (Eq. 5) with the overall mean temperature of the measuring periods (24.4 °C) used for estimating a_0 (see section 3.4).

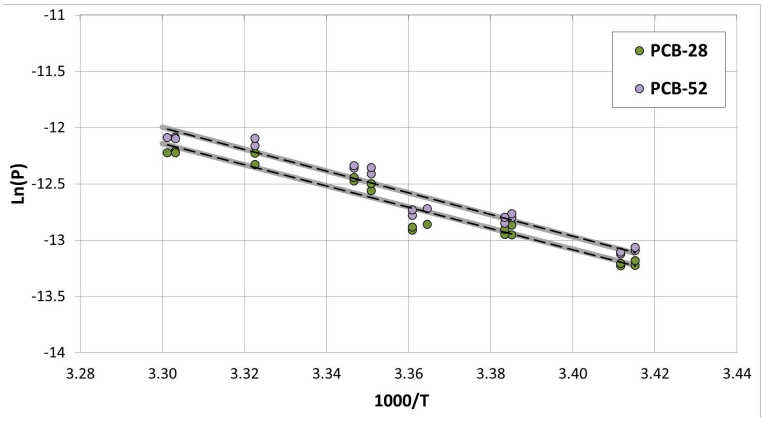


Figure 4.11 The models (grey lines), measured ln(P) [Pa] (dots) and their regression lines (dashed black lines) versus 1/T [K].

4.2.2 Additional field data

During the pilot remediation of an apartment in Farum Midtpunkt 98 PCB air samples was taken on 38 occasions. Concentrations (LnP) versus the inverse temperature, log-linear regression on the measured data and model predictions based on Clausius-Clapeyron Equation of the congeners PCB-52 and PCB-101 are shown in Figure 4.12. Results of PCB-28 are shown in Paper III. The models for the 3 detected congeners PCB-28, PCB-52 and PCB-101 are found to be within the 95% confidence interval of the ln(P) vs. 1/T regression.

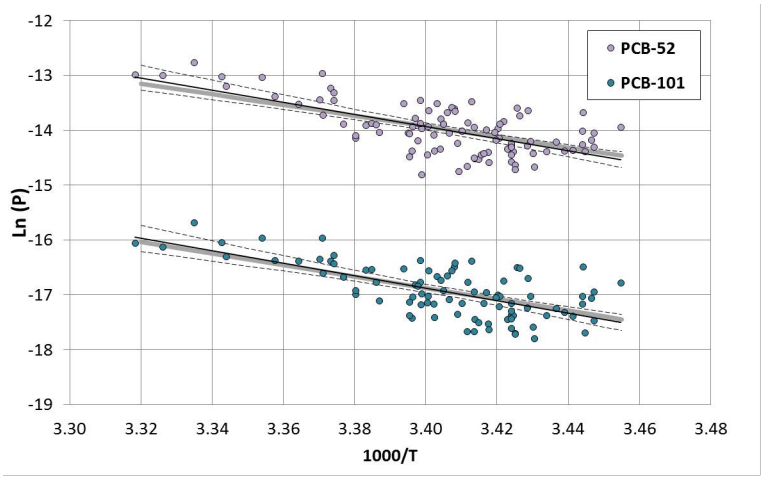


Figure 4.12 Measured ln(P) [Pa] (dots), their regression lines (thin black lines) with 95% confidence intervals and the models (thick grey lines) against 1/T [K].

4.2.3 Enthalpies of evaporation

Enthalpy of evaporation can be calculated from the regression slope of measured concentration (lnP) versus the inverse temperature. Figure 4.13 shows the calculated values with 95% confidence intervals and the reported values from Falconer and Bidleman (1994).

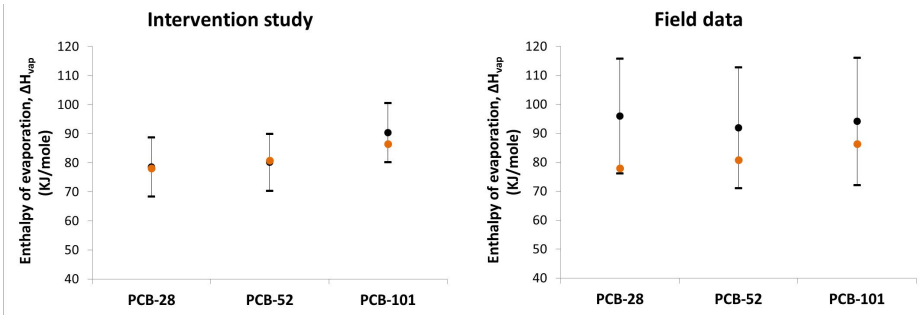


Figure 4.13 Reported (orange) and measured values with 95% CI (black) of enthalpy of evaporation, ΔH_{vap}.

4.3 Emission rates measured with test cells

The test cell build from a stainless steel food pan showed capable of measuring emission rates in both the laboratory and field. Steady state was reached as early as two days after the cell was placed on the surface. Within the first two weeks of measurements emission rates did not change significantly over time. During a longer period of time the laboratory test emission decreased significantly, most pronounced for the lower chlorinated congeners (Figure 4.15).

4.3.1 Laboratory testing

Air concentrations (Figure 4.14) and thereby emission rates were measured by the test cell from laboratory produced PCB paint in the laboratory. Two identical cells (A and B) were tested. Even though paint layer thickness was significantly different in the test cells, air concentration were not significantly different.

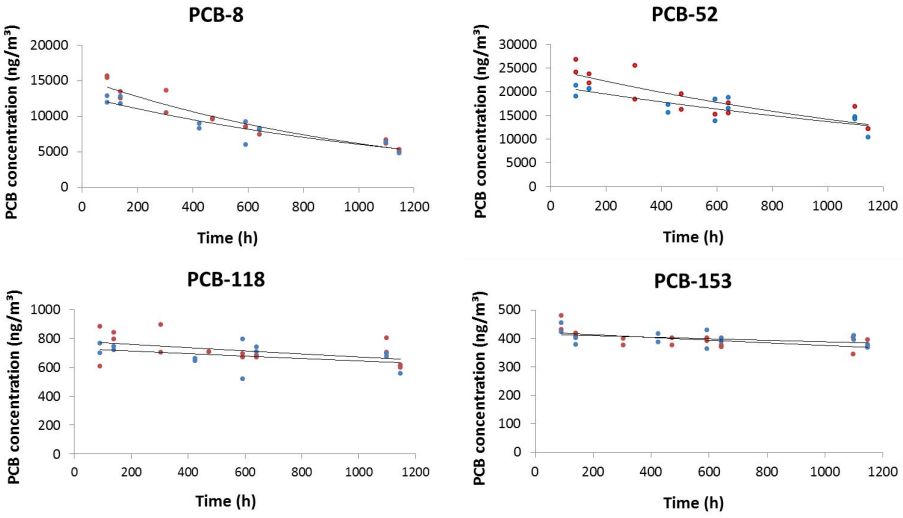


Figure 4.14 Air concentrations (ng/m³) as a function of time (h) for Cell A (blue) and Cell B (red) in laboratory tests and the exponential regression functions.

Figure 4.15, shows how the Specific Emission Rate (SER) of the detected congeners had decreased at Day 25 and at the last measurement (Day 48) relative to the first measurement (Day 4). One standard deviation of measurements are showed as uncertainties bars.

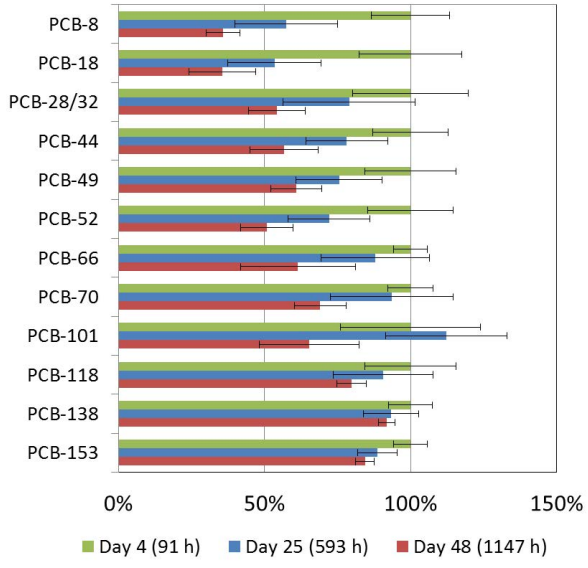


Figure 4.15 Decrease in SER of PCBs (%) on Day 25 and Day 48 relative to Day 4.

4.3.2 Field testing

The test cell was used to measure emission from 12 surfaces in 5 rooms in 2 different buildings. After SERs of 3 surfaces were measured in pairs (n=6) in the apartment building materials samples were collected from the measured surfaces. For PCB-52, PCB-101 and PCB-118 SER correlated with source concentration. SER versus source concentration of PCB-52, PCB-101 is shown in Figure 4.16.

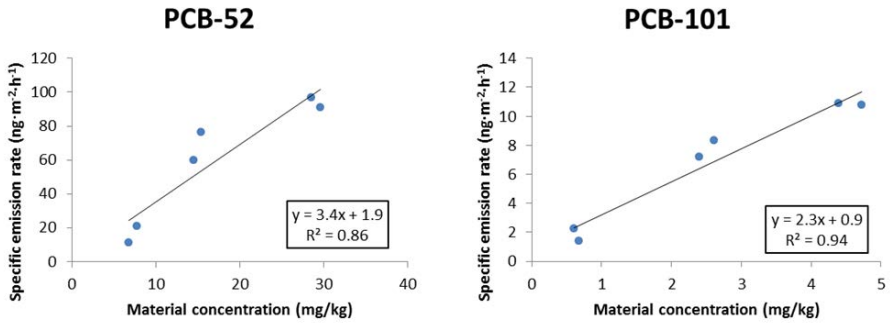


Figure 4.16 Correlation between material concentration and the specific emission rate from different building surfaces.

4.3.3 Comparison of room and test cell air concentrations

In 3 of the 5 rooms, air concentrations were measured shortly before or after the test cell measurements. Table 4.1 shows the room and cell air concentration and the temperature of the measurements.

Table 4.1 Room and test cell air concentrations and temperatures

		Test Cell	PCB_{total} Test cell air ng/m³	Test cell temperature[a] °C	PCB_{total} Room air ng/m³	Room air temperature °C
Bedroom	Wall	I	1683	24.1	3135	24.3
		II	1467			
	Floor	III	440			
		IV	247			
Teachers' office 1	Floor	C	567	18.2	190	21.4
	Wall + new caulk	D	60			
Teachers' office 2	Wall + new caulk	E	34	18.4	160	20.4
	Wall	F	51			

[a] Temperature was measured outside the test cell

In the bedroom the measured indoor air concentration is substantially higher than any of the test cell air concentrations. And in Teachers' office 1, test cell C placed

on the contaminated floor is higher than room air concentration. Air concentration in the other surfaces in Teachers' office 1 and 2 are mitigated surfaces which are reflected in the air concentrations.

5 Discussion

The discussion is focused on ventilation as a mitigation of PCB, the influence of temperature on concentration levels of PCB and the emission test cell as a tool for determining emission rates of PCB from building material.

5.1 Ventilation

In general increased ventilation had a reducing effect on indoor air concentrations of PCB. In this study, the reduction in concentrations was in average about 50% in case rooms and 30% in intervention rooms, however the reduction appeared to be strongly dependent of the specific building in question. When comparing case rooms within the same building where the initial concentrations were above 1000 ng/m^3 (Buildings 1, 4, 7 and 8 in Figure 4.1), the effects of ventilation resembled each other. This suggests that the decrease in concentration by ventilation obtained in one room may be applied to other similar rooms with same source characteristics within the same building. This was also the case for the two similar bedrooms in the intervention study.

In Building 2 and 5, the initial concentrations were relatively low (< 500 ng/m^3) and the effect of ventilation was not as pronounced as for the higher concentrations. In three rooms, concentration increased up to 80% with the increased ventilation. However, concentrations increased less than 150 ng/m^3, which could be caused by a variation due to other factors like cleaning condition of the room, outdoor temperature, sun and/or wind. In three case rooms (Building 4) the concentration decreased below the detection limit.

The large variation in the effect of the ventilation between buildings could also be caused by differences in ACHs. In most of the case rooms the ACHs were unknown. Increased ventilation had a greater effect (≥ 60% reduction) in 17 out of 26 case rooms compared with the intervention rooms (≤ 46% reduction), even though the large ACHs (> 4 h^{-1}) in the intervention rooms most likely exceed the ACH of the case rooms. However, in the ventilation intervention study in the bedrooms with four different ACHs, the largest decrease in concentration happened when ACH is increased from 0.5 to 2.2 h^{-1}, whereas additional increase in the ACH had little or no significant effect on concentration (Figure 4.4).

In the ventilation intervention study, the bulk air concentration (PCB_{total}) in the classroom decreased 30%, when turning on the mechanical ventilation and thus changing the ACH from 0.2 to 5.5 h^{-1}. From Eq. 2 it is seen that the emission rate increased by a factor of 18. In the bedrooms the emission rate of PCB-28 increased by a factor of 7.5 and 9.7 respectively, from no mechanical ventilation, ACH of 0.5 h^{-1}, to the highest level of mechanical ventilation, ACH of 6.6 h^{-1}. Emission rate in the intervention bedrooms increased linearly with increasing ACH. Emission in

bedrooms increased from ACHs of 4.5 to 6.6 h^{-1} without a significant change in room/bulk air concentration. Consequently the increased emissions must solely be due to a change in the convective mass transfer coefficient, h_m (Eq. 3), likely due to increased air velocity and possibly turbulence close to source surfaces (Sissom and Pitts, 1972). The increase in h_m indicated that no effect is achieved for additional increase in ventilation at high ACH resulting in increased air velocities as long as the source still has a potential to increase the emission rate.

The convective mass transfer coefficient h_m was estimated, based on an assumption of the concentration immediately above the source C_{ai} (section 4.1.3). In Figure 4.9 it appears that the increased concentration gradient at the first ventilation increase (ACH: 0.5 → 2.2 h^{-1}) mainly was responsible for the increase in emission rate in Bedroom A. In Bedroom B both increasing h_m and concentration gradient appeared to affect emission at the lower ventilation rates (ACH: 0.5 → 2.2 h^{-1}) as is the case in both bedrooms when ACH was increased from 2.2 to 4.5 h^{-1}. Increasing h_m was mainly responsible for the increase in emission rate at the high ACH (ACH: 4.5 → 6.6 h^{-1}) especially for the dominating congeners: PCB-28 and PCB-52 in Bedrooms A and B. These circumstances applied to the assumption that C_{ai} is 25 % above C_g at ACH = 0.5 h^{-1}; however when varying C_{ai} between 10 % and 50 % above C_g at ACH = 0.5 h^{-1} the same circumstances as seen for 25 % above C_g at ACH = 0.5 h^{-1} applied. This strengthens the assumption, that these circumstances were true. However the considerations was in fact based on assumptions, since it was not possible to evaluate the complex impact of h_m versus concentration gradient on the emission increase directly in other than the highest ventilation increase (ACH: 4.5 → 6.6 h^{-1}) where C_g was unaffected.

In the ventilation-intervention bedrooms and classroom, primary sources and partly secondary sources were encapsulated. In the classroom and bedrooms the large surface tertiary sources were believed to determine the steady-state bulk air concentration. The concentration, C_{ai}, immediately above tertiary source was most likely low compared with C_{ai} above primary sources containing PCB in percentages of the weight, since vapour pressure in combination with material concentration controls C_{ai} for SVOCs (Liang and Xu, 2014). It could be hypothesized that a relatively small increase in ACH without increasing the mass transfer coefficient in rooms where primary sources determine the steady-state bulk air concentration, C_g, could in fact decrease bulk air concentration. C_g could probably by means of ventilation be reduced to a level near C_{ai} of secondary and tertiary sources, without increasing emission. Since C_g *needs to be lower than* C_{ai} of secondary and tertiary sources before PCBs are emitted from these sources and emission from primary sources is likely unaffected by a change in C_g since primary source $C_{ai} >> C_g$. However, the convective mass transfer coefficient needs to be unaffected by the increase in ventilation for this hypothesis to work. Thereby the emission rate could be less affected by increase in ACH compared with cases with remediated primary sources. Therefore increased ventilation as mitigation could be more effective in

cases with intact primary sources. However this hypothesis was not investigated in this study and thus could not be substantiated at this point.

There is very sparse literature on the effect of ventilation on concentration of PCB in indoor air. VDI (2009) recommends increased ventilation as a possible mitigating measure on elevated PCB concentrations. Decreasing concentrations due to increase in ventilation is also found by MacIntosh et al. (2012), unfortunately the actual ACHs are unknown. Liang and Xu (2015) found a linear increase in emission for another SVOC (di-2-ethylhexyl-phthalate, DEHP) based on three different ACHs (16, 56 and 156 h^{-1}) in a chamber study with vinyl flooring (23% DEHP). The study substantiates the linear increase in PCB emission as found in the intervention study, even though ACHs for DEHP is much higher. However, published results of model calculations of the effect of ventilation on concentrations by Liu et al. (2014) and Thomas et al. (2012) predicts a larger effect of the ventilation on decrease in air concentration than found in this study. However, the model simulations are based on SVOC emissions from primary sources, whereas this intervention study investigate the effect of ventilation on concentrations caused by emissions from secondary and tertiary sources, since primary sources (caulks) and partly secondary sources were encapsulated in the three intervention room.

Based on 4 rooms with PCB caulks in Paper I, the differential pressure between the room and the surrounding appeared to have an impact on the PCB emission to the room. Even though data were limited this occurrence seemed plausible, since change in concentration might be explained by ex- and infiltration respectively, possibly at cracks and gaps often at the position of caulks. Airflows in these areas might result in change in the convective mass transfer as well as movement of highly contaminated air to or from the room.

5.2 Temperature

Several studies have reported the impact of temperature on PCB emission and concentration in in- and outdoor air and increasing concentrations at increasing temperature is well documented (Halsall et al., 1999; Bent et al., 2000; Carlson and Hites, 2005; Kohler et al., 2005). The temperature intervention study and the additional field data showed a log-linear correlation with the inverse temperature corresponding to a few other studies (Halsall et al., 1999; U.S. EPA 2011).

The Clausius-Clapeyron equation (Eq. 5), which specifies the physicochemical correlation between vapour pressure and temperature, was used in this study to describe the relation between air concentrations and temperature. Estimation of a_0, was based on measurements of air concentration, expressed as partial pressure ($\ln P$) vs. air temperature ($1/T$) and values of enthalpy of evaporations (ΔH) was from Falconer and Bidleman (1994). When the Clausius-Clapeyron equation (Eq. 5)

was used on measured air concentrations (ln*P*) and air temperature from one bedroom (intervention study) and one apartment (additional data) it was found not significantly different from the regression of measured air concentrations (ln*P*) vs. air temperature (1/*T*) in the temperature intervention study (R^2> 94%) and the additional field data (R^2> 44%). Thus enthalpy of evaporation from Falconer and Bidleman (1994) corresponded with the enthalpy of evaporation retrieved from the temperature intervention study and the field measurements (Figure 4.13). This means that with a set of assumptions the concentrations of PCB in indoor air and the relation to air temperature were in accordance with the predictions based on the Clausius-Clapeyron equation (Eq. 5). The assumptions included constant source concentration, steady-state air concentrations, source and air temperatures as well as low influence of other factors such as direct sun and change in ACH.

Air temperatures indoors are rarely homogenous and air and material temperature may very well differ due to outdoor temperature, sun and indoor heating/cooling. Temperature fluctuations can appear faster in air compared with material temperatures due to the low heat capacity of air. In the intervention study the steady-state air and surfaces temperature were comparable and fairly homogenously. In the additional field data study the surface temperatures were unknown. Therefore the effect of air versus surface temperature on air concentrations was inseparable in this study. Since PCBs are categories as SVOCs, emissions of PCBs are believed to be controlled by external emission mechanisms such as diffusion in the air boundary layer adjacent to the source instead of the internal mechanism of diffusion in the material (Xu and Little, 2006). This means that the emission is controlled among other things by the air diffusion coefficient and thus correlated with $T^{1.5}$ (Sissom and Pitts, 1972). However emission increased exponentially with increasing temperature and is likely controlled by the partitioning between solid (source) and gas-phase and/or evaporation of PCBs from the source, where source temperature affect the emission rate. This complex boundary layer phenomenon was not investigated thoroughly in this study. Nevertheless air temperature in the middle of the room appears to works as a good indicator of the emission rate in this study.

The method used for temperature adjustment of concentrations in the investigation of the effect of ventilation (Paper I and II) could be justified by the temperature investigations in Paper III. The used method based on concentrations in ng/m³ rather than partial pressures (Pa) resulted in a margin of error of less than 2.3% when adjusting for a temperature difference of up to 6.7 °C (the largest temperature adjustment) compared with partial pressures. Concentrations from the field intervention studies with mechanical ventilation still varied after the temperature adjustments especially in the classroom. This could be caused by other influencing factors such as different source temperature, outdoor temperature and impact of wind.

5.3 Emission Test Cell

It was possible to develop an emission test cell that was robust and portable at a low cost (less than US $ 150). The developed emission test cell showed capable of measuring emission rates from several very different surfaces with Specific Emission Rates, SERs varying between just above the detection limit of 0.08 ng/(m²·h) and up to 4000 ng/(m²·h). Sorption on test cell surfaces did not influence measurements after 2-4 days after placement on source surface. This was fast compared with emission rate measurements of DEHP (another SVOC) in the FLEC, where time to steady state has been shown to take months (Clausen et al., 2004). Therefore, the emission test cell could be used to evaluate source strength of different types of surfaces in order to prioritize remediation measures within a realistic timeframe of days.

Emission rates measured in contaminated buildings did not decrease within a measuring period of 2 weeks in the experiments conducted in this study. However, emission rates from the stainless steel plates painted with freshly made PCB containing paint decreased over a longer period of time (48 days). The relative decrease for the single congeners was depended on the degree of chlorination. For the lower chlorinated PCBs (<5 chlorine atoms) emission rates decreased rapidly, whereas for the higher chlorinated congeners (PCB-118, PCB-138 and PCB-153) it did not or only marginally decreased.

Measurements showed that different PCB containing materials have different source strengths, since SER varied greatly between different types of indoor surfaces even within the same room. Test cell concentrations were measured to be below the concentration in room air which was measured immediately before or after the test cell measurements. This indicates how adsorption to the surfaces can change to desorption when these were exposed to clean air, thus surfaces changed from sinks to sources. These results substantiate findings from laboratory emission measurements of PCB performed by EPA (U.S. EPA, 2011; 2012a) and have been reported from other organic compounds as well (Berglund et al. 1989; Tichenor et al. 1991). Tichenor et al. (1991) found the sink strength of an indoor surface, thus the ability of the surface to absorb compounds, is different for different surface materials and dependent on the absorbed compound.

Parallel emission rate measurement carried out pairwise on similar painted plates, the same bedroom wall and the same corridor wall was not significantly different between the pairwise measurements. Parallel emission rate measurement from bedroom floor varied up to 60% and this difference was not reflected by source surface concentrations.

Six parallel emission rate measurement from three different surfaces: corridor wall, bedroom wall and floor showed that the emission rate was somewhat controlled by the concentration in the emitting source. Three of the six detected congeners (PCB-52, PCB-101 and PCB-118) correlated linearly with source concentrations. For the three remaining detected congeners: PCB-28, PCB-138 and PCB-153 no correlation was found with the concentration in the source. However PCB-138 and PCB-153 were measured in concentrations close to the detection limit, which enhances the analytic uncertainty. Guo et al. also found SER of PCB-52 linear correlated with the concentration in the source (U.S. EPA, 2011).

The field emission rate measurements in the Fourfeldt School (Fourfeldtskolen) in Paper IV included emission rates for three different remediated surfaces. Measurements indicate how the test cell can be used to test the effect of remediation measures of small surface sections in situ. Thus, remediation measures can be tested in small scale, before whole building or building sections is remediated. Control measurements performed shortly after the remediation have been completed does not reveal the effect of the remediation over time. Encapsulation might possibly become less effective over time due to diffusion in the encapsulating material. However increased temperature and possibly increased ventilation over a period of time might eventually desorb PCBs from tertiary contaminated surfaces to a degree where the source strength is decreased.

The measured emission rates were only tentative in relation to the actual emission rate for the building surface in the room without the test cell attached, since emission is affected by factors such as bulk air concentration, ventilation rate, air velocity and presumably particles. The measured emission rate reflected the potential of the source, if all other sources were removed; i.e. the surface was the only source to the room air content of PCB. If different emissions rates are measured in the same room the emission measurements can help prioritize and plan remediation measures by the indication of the source potential of the surface.

6 Conclusion

The main conclusions of this study were:

Ventilation

- Increased ventilation reduces PCB concentration in indoor air in most cases
- The reducing effect of the ventilation varies from case to case
- Emission rates of PCBs increases linearly with increasing air exchange rate in two studied bedrooms

Temperature

- Increased source/air temperature increase air concentration of PCB exponentially
- Model predictions of the variation in concentration due to changed air temperature based on Clausius-Clapeyron equation is found within the confidence interval of the concentration, ln(P) vs. air temperature, 1/T regression
- With a certain set of assumptions steady-state air concentrations at steady-state temperatures can be modelled by the Clausius-Clapeyron equation and at least one reference point (a steady-state concentration and the related temperature)

Emission test cell

- A low-cost emission test cell was developed and can be used to measure PCB-emission rates for building surfaces in situ on a short time scale (days)
- The test cell can be used in assessment of potential source strength at the specific measuring conditions for ACH, temperature and clean inlet air and thereby help prioritise and test remediation measures
- Different types of PCB containing materials have different emission rates even within the same room

7 Perspectives

This study is not an in-depth investigation of boundary layer emission mechanisms and further investigations are needed to achieve a better understanding of emission mechanisms. The effect of air velocity on convective mass transfer should be investigated as this alone can affect the emission and concentration of PCB in indoor air. In addition the influence of differential pressure on air concentration should be investigated in order to substantiate the findings based on four case rooms that found differential pressure to affect the air concentration. Also the effect of increased ventilation on the air concentration in cases with primary sources with high content of PCB should be investigated. More emission test cell measurements should be done in order to investigate the effect of different area specific ventilation rates on surface emission rates.

Investigation of the effect of humidity, particles and dust on emission of PCB from building material was beyond the scope of this study. Normal indoor humidity conditions are not assumed to affect the emissions of PCB, nor does humidity influence emissions of DEHP (Clausen et al., 2007). Particles and dust have been reported to affect the emission and air concentration of SVOC including PCB in laboratory studies and models (Xu and Little, 2006; Liu et al., 2012; U.S. EPA 2012a; Benning et al., 2013). The impact of particulate matter and dust on emissions of PCBs in indoor environments should be investigated too.

After a change in temperature or ventilation rate in a room, the steady-state PCB concentration in air is reached rapidly (within days or even hours) compared with other SVOCs such as DEHP. The same is true for steady-state air concentration in the test cell. Knowledge of the hourly variation in concentration of PCB as well as day to day variation is limited and should be explored in order to quantify the exposure of occupants in contaminated buildings.

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